PB87-146700

Alternative Disinfectants and Granular Activated Carbon Effects on Trace Organic Contaminants

Jefferson Parish Dept. of Public Utilities, LA

Prepared for

Environmental Protection Agency, Cincinnati, OH

Jan 87

U.S. Department of Commerce
National Technical Information Service
NTIS

PB87-146700

EPA/600/2-87/006
January 1987

ALTERNATIVE DISINFECTANTS AND GRANULAR ACTIVATED CARBON EFFECTS ON TRACE ORGANIC CONTAMINANTS

by

Wayne E. Kottskey
Department of Public Utilities
Jefferson Parish
Jefferson, Louisiana 70121

Coope[illegible]ve Agreement No. CS805925

Project Officer

Ben Lykins, Jr.
Drinking Water Research Division
Water Engineering Research Laboratory
Cincinnati, Ohio 45268

WATER ENGINEERING RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U. S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA/600/2-87/006

2.

3. RECIPIENT'S ACCESSION NO.
PB87 146700/AS

4. TITLE AND SUBTITLE
Alternative Disinfectants and Granular Activated Carbon Effects on Trace Organic Contaminants

5. REPORT DATE
January 1987

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
Wayne E. Koffskey

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Jefferson Parish Department of Public Utilities
Jefferson, Louisiana 70121

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.
CS806925

12. SPONSORING AGENCY NAME AND ADDRESS
Water Enginnering Research Laboratory-Cincinnti, OH
Office of Research and Development
U.S Environmental Protection Agency
Cincinnati, OH 45268

13. TYPE OF REPORT AND PERIOD COVERED
Final report (5/83-5/84)

14. SPONSORING AGENCY CODE
EPA/600/14

15. SUPPLEMENTARY NOTES
Project Officer - Benjamin W. Lykins, Jr. (513/569-7460)

16. ABSTRACT

The effects of alternative disinfectants on drinking water quality were examined along with the ability of granular activated carbon (GAC) to remove disinfection by-products and organic contaminants from lower Mississippi River source water. In addition, the study obtained bacteriological information associated with the influent and effluent of each sand and GAC column, and it evaluated the effects of post filtration disinfection with monochloramine and free chlorine. One other objective was to collect water samples for health effects research.

To accomplish these objectives, four parallel pilot column process streams were each dosed with a different disinfectant (ozone, chlorine dioxide, monochloramine, and chlorine) and compared with a fifth pilot column stream that was not disinfected. After 30 min of disinfectant contact time, each process stream was passed through parallel sand, GAC and duplicate GAC filters, each with 20 min of empty bed contact time. In addition, separate aliquots of the effluent of each pilot column were dosed with monochloramine and free chlorine and then dechlorinated after 5 days of incubation at river water temperature.

Samples collected from each step in each process stream were analyzed for total organic carbon, total organic halide, 10 volatile organics, 65 solvent-extractable hydrocarbons, 26 chlorinated hydrocarbon insecticides, heterotrophic plate count, total coliforms, and dissolved oxygen.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT
RELEASE TO PUBLIC

19. SECURITY CLASS *(This Report)*
UNCLASSIFIED

20. SECURITY CLASS *(This page)*
UNCLASSIFIED

21. NO. OF PAGES
286

22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

DISCLAIMER

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under Assistance Agreement Number CS805925 to Jefferson Parish, Louisiana. It has been subject to the Agency's Peer and Administrative Review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

The U. S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water systems. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. The Clean Water Act, the Safe Drinking Water Act, and the Toxic Substances Control Act are three of the major congressional laws that provide the framework for restoring and maintaining the integrity of our Nation's Water, for preserving and enhancing the water we drink, and for protecting the environment from toxic substances. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Water Engineering Research Laboratory is that component of EPA's Research and Development program concerned with preventing, treating, and managing municipal and industrial wastewater discharges; establishing practices to control and remove contaminants from drinking water and to prevent its deterioration during storge and distribution; and assessing the nature and controllability of releases of toxic substances to the air, water, and land from manufacturing processes and subsequent product uses. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

This study reports on a cooperative research effort that examines alternative disinfection methods in conjunction with granular activated carbon filtration for minimizing organic contaminants in drinking water from the lower Mississippi River. The formation of disinfection by-products by ozone, chlorine dioxide, chloramine, and chlorine was evaluated on a pilot scale along with the ability of granular activated carbon to remove these byproducts in conjunction with the existing organic contaminants present in the source water.

Francis T. Mayo, Director
Water Engineering Research Laboratory

ABSTRACT

The effects of alternative disinfectants on drinking water quality were examined along with the ability of granular activated carbon (GAC) to remove disinfection by-products and organic contaminants from lower Mississippi River source water. In addition, the study obtained bacteriological information associated with the influent and effluent of each sand and GAC column, and it evaluated the effects of post filtration disinfection with monochloramine and free chlorine. One other objective was to collect water samples for health effects research.

To accomplish these objectives, four parallel pilot column process streams were each dosed with a different disinfectant (ozone, chlorine dioxide, chloramine, and chlorine) and compared with a fifth pilot column stream that was not disinfected. After 30 min of disinfectant contact time, each process stream was passed through parallel sand, GAC and duplicate GAC filters, each with 20 min of empty bed contact time. In addition, separate aliquots of the effluent of each pilot column were dosed with monochloramine and free chlorine and then dechlorinated after 5 days of incubation at river water temperature.

Samples collected from each step in each process stream were analyzed for total organic carbon, total organic halide, 10 volatile organics, 65 solvent-extractable hydrocarbons, 26 chlorinated hydrocarbon insecticides, heterotrophic plate count, total coliforms, and dissolved oxygen.

The most efficient process train for minimizing dissolved organic contaminants in lower Mississippi River drinking water was predisinfection with ozone followed by GAC filtration and post disinfection with chloramines. The second most efficient treatment train was GAC filtration followed by postdisinfection with chloramines without any predisinfection.

This report was submitted in fulfillment of Cooperative Agreement No. CS806925 by Jefferson Parish, Louisiana, under the sponsorship of the U.S. Environmental Protection Agency. This report covers the operational period from May 1983 through May 1984.

CONTENTS

Foreword iii
Abstract iv
Figures vi
Tables xviii
Abbreviations xxi
Metric Conversion Table xxv
Acknowledgments xxvi

1. Introduction 1
2. Conclusions 3
3. Recommendations 5
4. Pilot Column Configuration 6
5. Sampling, Analysis, and Quality Assurance 12
6. Operational Parameters and Conditions . . 41
7. Results and Discussion 71
    TOC 71
    TOX 74
    Trihalomethanes 99
    1,2-Dichloroethane 124
    Other Volatile Organics 125
    Atrazine 125
    Alachlor 131
    Total Chlorinated Hydrocarbon Insecticide 139
    Total Alkylbenzene 146
    Total Alkane 151
    Total Phthalate 159
    Total PNAH 168
    Total Chlorobenzene 177
    Total Nitrobenzene 179
    Total Alkylaldehyde 185
    Other Semivolatile Organics 192
    Disinfection By-products 195
    Summary of the Effects of Predisinfection and GAC Filtration on Average Water Quality 237

References 244
Appendix. Granular Activated Carbon Selection 245

FIGURES

NUMBER		PAGE
1	Pilot column system flow schematic	7
2	Detailed schematic of each disinfectant process stream	8
3	Schematic of the underdrain system for each pilot column	9
4	Detailed schematic of the ozone contact chamber	11
5	Schematic of the sampling locations of the pilot column system	14
6	Comparison of identified peak area versus percent relative deviation of the duplicate solvent extractable chlorinated hydrocarbon insecticide analyses	32
7	Comparison of identified peak area versus percent relative deviation of the duplicate solvent extractable hydrocarbon analyses	33
8	Empty bed contact times observed for the nondisinfected process stream	44
9	Empty bed contact times observed for the ozone process stream	45
10	Empty bed contact times observed for the chlorine dioxide process stream	46
11	Empty bed contact times observed for the chloramine process stream	47
12	Empty bed contact times observed for the chlorine process stream	48

FIGURES

NUMBER PAGE

13 Ozone residuals in the influent water of the ozone system after 30 minutes of disinfectant contact time 52

14 Chlorine dioxide and chlorite residuals in the influent water of the chlorine dioxide system after 30 minutes of disinfectant contact time 53

15 Free chlorine, monochloramine, and dichloramine residuals in the influent water of the chlorine dioxide system after 30 minutes of disinfectant contact time 54

16 Free chlorine, monochloramine, and dichloramine residuals in the influent water of the chloramine system after 30 minutes of disinfectant contact time . 55

17 Free chlorine, monochloramine, and dichloramine residuals in the influent water of the chloramine system after 30 minutes of disinfectant contact time 56

18 Temperature of the nondisinfected influent water entering the pilot column system 59

19 Comparison of the average geometric means of total bacteria (heterotrophic plate count) for the influent and effluent locations of each process stream . . . 60

20 Comparison of the heterotrophic plate count in the effluents of each sand column . 61

21 Comparison of the average dissolved oxygen levels in the influent and effluent of each process stream 63

22 Comparison of the average change in dissolved oxygen in the influent and effluent of each process stream 64

FIGURES

NUMBER PAGE

23 Comparison of the TOC influent levels for each process stream 72

24 Comparison of the TOC sand effluent levels for each process stream 73

25 Comparison of the TOC GAC and GAC duplicate effluent levels for each process stream 75

26 Comparison of the TOC reductions observed across each GAC and GAC duplicate column 76

27 TOC breakthrough profiles for the nondisinfected process stream 77

28 TOC breakthrough profiles for the ozone process stream 78

29 TOC breakthrough profiles for the chlorine dioxide process stream 79

30 TOC breakthrough profiles for the chloramine process stream 80

31 TOC breakthrough profiles for the chlorine process stream 81

32 Comparison of the TOX influent levels for each process stream 82

33 Comparison of the TOX sand effluent levels for each process stream 85

34 Comparison of the TOX GAC and GAC duplicate effluent levels for each process stream 86

35 Comparison of the TOX reductions observed across each GAC and GAC duplicate column 87

36 TOX breakthrough profiles for the nondisinfected process stream 88

FIGURES

NUMBER PAGE

37 TOX breakthrough profiles for the ozone process stream 89

38 TOX breakthrough profiles for the chlorine dioxide process stream 90

39 Tox breakthrough profiles for the chloramine process stream 91

40 TOX breakthrough profiles for the chlorine process stream 92

41 Average terminal TOX-Cl_2 levels after the addition of free chlorine and storage for 5 days at 28°c 94

42 Comparison of the TOX-Cl_2 GAC effluent levels for each process stream 96

43 Average terminal TOX-NH_2Cl levels after the addition of monochloramine and storage for 5 days at 28°c 97

44 Comparison of the TOX-NH_2Cl GAC effluent levels for each process stream . . . 98

45 TOX-Cl_2 and TOX-NH_2Cl breakthrough profiles for the nondisinfected process stream 100

46 TOX-Cl_2 and TOX-NH_2Cl breakthrough profiles for the ozone process stream 101

47 TOX-Cl_2 and TOX-NH_2Cl breakthrough profiles for the chlorine dioxide process stream 102

48 TOX-Cl_2 and TOX-NH_2Cl breakthrough profiles for the chlorine and chloramine process streams 103

49 Comparison of the THM-T influent levels for each process stream 105

FIGURES

NUMBER PAGE

50 Comparison of the THM-I sand effluent levels for each process stream . . . 107

51 Comparison of the THM-I GAC and GAC duplicate effluent levels for each process stream 108

52 Comparison of the THM-I reductions observed across each GAC and GAC duplicate column 109

53 THM-I breakthrough profiles for the nondisinfected process stream 110

54 THM-I breakthrough profiles for the ozone process stream 111

55 THM-I breakthrough profiles for the chlorine dioxide process stream . . . 112

56 THM-I breakthrough profiles for the chloramine process stream 113

57 THM-I breakthrough profiles for the chlorine process stream 114

58 Average terminal THM-Cl_2 levels after the addition of free chlorine and storage for 5 days at 28°c 115

59 Comparison of the THM-Cl_2 GAC effluent levels for each process stream . . . 117

60 Average terminal THM-NH_2Cl levels after the addition of free chlorine and storage for 5 days at 28°c 118

61 Comparison of the THM-NH_2Cl GAC effluent levels for each process stream . . . 119

62 THM-Cl_2 and THM-NH_2Cl breakthrough profiles for the nondisinfected process stream 121

FIGURES

NUMBER		PAGE
63	THM-Cl_2 and THM-NH_2Cl breakthrough profiles for the ozone process stream	122
64	THM-Cl_2 and THM-NH_2Cl breakthrough profiles for the chlorine dioxide process stream	123
65	THM-Cl_2 and THM-NH_2Cl breakthrough profiles for the chlorine and chloramine process streams	124
66	Comparison of the 1,2-dichloroethane influent and sand effluent levels for each process stream	126
67	Comparison of the 1,2-dichloroethane GAC and GAC duplicate effluent levels for each process stream . . .	127
68	1,2-dichloroethane breakthrough profiles for the nondisinfected and chlorine process streams	128
69	Comparison of the atrazine influent levels for each process stream	129
70	Comparison of the atrazine sand effluent levels for each process stream . . .	130
71	Atrazine breakthrough profiles for the ozone process stream	132
72	Comparison of the atrazine GAC and GAC duplicate effluent levels for each process stream	133
73	Atrazine breakthrough profiles for the nondisinfected process stream	134
74	Comparison of the alachlor influent levels for each process stream . . .	135
75	Comparison of the alachlor sand effluent levels for each process stream . . .	136

FIGURES

NUMBER		PAGE
76	Alachlor breakthrough profiles for the ozone process stream	137
77	Comparison of the alachlor GAC and GAC duplicate effluent levels for each process stream	138
78	Alachlor breakthrough profiles for the chloramine process stream . . .	140
79	Comparison of the total CHI influent levels for each process stream . . .	141
80	Comparison of the total CHI sand effluent levels for each process stream . .	142
81	Total CHI breakthrough profiles for the ozone process stream	143
82	Comparison of the total CHI combined GAC effluent levels for each process stream	144
83	Total CHI breakthrough profiles for the chlorine dioxide process stream	145
84	Comparison of the total alkylbenzene influent levels for each process stream	147
85	Comparison of the total alkylbenzene sand effluent levels for each process stream	149
86	Total alkylbenzene breakthrough profiles for the ozone process stream	150
87	Comparison of the total alkylbenzene GAC and GAC duplicate effluent levels for each process stream	152
88	Total alkylbenzene breakthrough profiles for the nondisinfected process stream	153

FIGURES

NUMBER		PAGE
89	Total alkylbenzene breakthrough profiles for the chlorine dioxide and chloramine process streams	154
90	Total alkylbenzene breakthrough profiles for the chlorine process stream . .	155
91	Comparison of the total alkane influent levels for each process stream . .	156
92	Comparison of the total alkane sand effluent levels for each process stream	157
93	Total alkane breakthrough profiles for the ozone process stream	158
94	Comparison of the total alkane GAC and GAC duplicate effluent levels for each process stream	159
95	Total alkane breakthrough profiles for the chlorine process stream	161
96	Comparison of the total phthalate influent levels for each process stream	162
97	Comparison of the total phthalate sand effluent levels for each process stream	164
98	Comparison of the total phthalate GAC and GAC duplicate effluent levels for each process stream	165
99	Total phthalate breakthrough profiles for the nondisinfected process stream	166
100	Total phthalate breakthrough profiles for the ozone process stream . . .	167
101	Total phthalate breakthrough profiles for the chlorine dioxide process stream	169

FIGURES

NUMBER PAGE

102 Total phthalate breakthrough profiles for the chloramine and chlorine process streams 170

103 Comparison of the total PNAH influent levels for each process stream . . 171

104 Comparison of the total PNAH sand effluent levels for each process stream . . 172

105 Total PNAH breakthrough profiles for the ozone process stream 173

106 Comparison of the total PNAH GAC and GAC duplicate effluent levels for each process stream 174

107 Total PNAH breakthrough profiles for the nondisinfected process stream . . . 175

108 Total PNAH breakthrough profiles for the chlorine dioxide process stream . . 176

109 Comparison of the total chlorobenzene influent levels for each process stream 178

110 Comparison of the total chlorobenzene sand effluent levels for each process stream 180

111 Total chlorobenzene breakthrough profiles for the chlorine process stream . . 181

112 Total chlorobenzene breakthrough profiles for the ozone process stream . . . 182

113 Comparison of the total chlorobenzene GAC and GAC duplicate effluent levels for each process stream 183

114 Total chlorobenzene breakthrough profiles for the chlorine dioxide process stream 184

FIGURES

NUMBER		PAGE
115	Comparison of the total nitrobenzene influent levels for each process stream	186
116	Comparison of the total nitrobenzene sand effluent levels for each process stream	187
117	Comparison of the total nitrobenzene GAC and GAC duplicate effluent levels for each process stream . .	188
118	Total nitrobenzene breakthrough profiles for the chloramine process stream .	189
119	Comparison of the total alklaldehyde influent levels for each process stream	190
120	Comparison of the total alkylaldyhyde sand and GAC effluent levels for each process stream	191
121	Tributylphosphate breakthrough profiles for the ozone process stream . . .	193
122	Triphenylmethane breakthrough profiles for the chlorine dioxide process stream	194
123	4-nonylphenol breakthrough profiles for the chlorine process stream	195
124	d-Fenchone breakthrough profiles for the ozone and chlorine process streams	197
125	d-Fenchone breakthrough profiles for the chlorine dioxide process stream . .	198
126	Typical flame ionization GC profiles of the influent locations of each process stream obtained on day 87	201

FIGURES

NUMBER		PAGE
127	Typical electron capture GC profiles of the influent locations of each process stream obtained on day 87	203
128	Total flame ionization concentrations in the influent of each process stream	206
129	Total electron capture concentrations in the influent of each process stream	207
130	Typical flame ionization GC profiles of the sand column effluent of each process stream obtained on day 87	209
131	Typical electron capture GC profiles of the sand column effluent of each process stream obtained on day 87	210
132	Total flame ionization concentrations in the sand column effluent of each process stream	212
133	Total electron capture concentrations in the sand column effluent of each process stream	213
134	Flame ionization GC profiles of the GAC column effluent of each process stream during the first week of operation	215
135	Flame ionization GC profiles of the GAC column effluent of each process stream after 3 months of operation	217
136	Flame ionization GC profiles of the GAC column effluent of each process stream after 6 months of operation	219
137	Flame ionization GC profiles of the GAC column effluent of each process stream after 9 months of operation	221
138	Flame ionization GC profiles of the GAC column effluent of each process stream after 12 months of operation . . .	223

FIGURE

NUMBER PAGE

139 Total flame ionization concentrations in the effluent of the GAC and GAC duplicate columns of each process stream . . 225

140 Electron capture GC profiles of the GAC column effluent of each process stream during the first week of operation 226

141 Electron capture GC profiles of the GAC column effluent of each process stream after 3 month of operation 228

142 Electron capture GC profiles of the GAC column effluent of each process stream after 6 months of operation 230

143 Electron capture GC profiles of the GAC column effluent of each process stream after 9 months of operation . . . 232

144 Electron capture GC profiles of the GAC column effluent of each process stream after 12 months of operation . . . 234

145 Total electron capture concentrations in the combined GAC and GAC duplicate effluents of each process stream 236

TABLES

NUMBER		PAGE
1.	Pilot column system sampling and analysis schedule	13
2.	Gas chromatography standard concentrations and detection limits for volatile organics analysis	15
3.	Gas chromatography standard concentrations, detections limits, and percent recoveries for solvent extractable hydrocarbon analysis	15
4.	Gas chromatography standard concentrations, detection limits, and percent recoveries for chlorinated hydrocarbon insecticide analysis	17
5.	GC/MS standard concentrations, recoveries and detection limits for volatile organic confirmation via grob analysis	23
6.	GC/MS standard concentrations, recoveries, and detection limits for solvent extractable hydrocarbon confirmation	23
7.	GC/MS standard concentrations, recoveries, and detection limits for chlorinated hydrocarbon insecticide confirmation . . .	25
8.	Analytical precision as measured by duplicate sample analysis	29
9.	Analytical accuracy as measued by internal quality control sample analysis	34
10.	USEPA performance evaluation standards WS012, May 1983	35

TABLES

NUMBER PAGE

11. USEPA performance evaluation standards WS013, October 1983 35

12. USEPA performance evaluation standards WS014, May 1984 36

13. Percent of possible GC/MS confirmation and average mass spectral fit of volatile organics and solvent extractable hydrocarbons in the influent of each process stream 38

14. Percent of possible GC/MS confirmation and average mass spectral fit of chlorinated hydrocarbon insecticides in the influent of the nondisinfected process stream 40

15. Physical operating conditions for the pilot column system during the first year of operation 43

16. Average water quality of nondisinfected influent water to the pilot column system after pressure sand filtration 50

17. Average thirty minute disinfectant demands and residuals 50

18. Comparison of average thirty minute disinfectant residuals of each disinfectant process stream 57

19. Frequency of occurrence of various gram negative bacteria for the influent water to each pilot column of each process stream 66

20. Frequency of occurrence of various gram negative bacteria for the effluent of the sand columns of each process stream . . . 67

21. Frequency of occurrence of various gram negative bacteria for the effluent of the GAC columns of each process stream . . . 68

22. Frequency of occurrence of various gram negative bacteria for the effluent of the GAC duplicate columns of each process stream 69

TABLES

NUMBER PAGE

23. Average total coliform data for each sampling location of the pilot column system 70

24. Frequency of occurrence and concentration ranges in the nondisinfected influent of chlorinated hydrocarbon insecticides comprising total CHI 145

25. Frequency of occurrence and concentration ranges of alkylbenzenes in the nondisinfected influent comprising total alkylbenzenes . 148

26. Frequency of occurrence and concentration ranges of normal alkanes in the nondisinfected influent comprising total alkane 160

27. Frequency of occurrence and concentration ranges of phthalates in the nondisinfected influent comprising total phthalate . . . 163

28. Frequency of occurrence and concentration ranges of PNAH in the nondisinfected influent comprising total PNAH 177

29. Frequency of occurrence and concentration ranges of chlorobenzene in the nondisinfected influent comprising total chlorobenzene . 179

30. Primary by-products identified in the influent of each disinfected process stream and confirmed by external standards 200

31. Summary of the effects of the alternative disinfectants over the one year operational period 238

32. Summary of the combined effects of the alternate disinfectants and sand filtration over the one operational period 239

33. Summary of the combined effects of the alternative disinfectants and GAC filtration over the one year operational period . . 240

LIST OF ABBREVIATIONS

AMU	-- atomic mass units
ave	-- average
^{o}C	-- degree centigrade
CFU	-- colony forming units
CGC	-- capillary gas chromatography
$CHBr_3$	-- bromoform
$CHBrCl_2$	-- bromodichloromethane
$CHBr_2Cl$	-- dibromochloromethane
$CHCl_3$	-- chloroform
CHI	-- total chlorinated hydrocarbon insecticide
Cl_2	-- free chlorine
$-Cl_2$	-- free chlorine at ambient pH and temperature
ClO_2	-- chlorine dioxide
cm/sec	-- centimeters per second
cts/ml	-- counts per milliliter
cu ft	-- cubic foot
DCE	-- 1,2-dichloroethane
DCPA	-- dimethyl-1,2,3,5,6-tetrachloroterephthalate
DFTPP	-- decafluorotriphenylphosphine
DO	-- dissolved oxygen
DPD	-- n,n-diethyl-p-phenylenediamine

dupl -- duplicate

EBCT -- empty bed contact time

ECTOAR -- electron capture total area

effl -- effluent

EMSL -- EPA Envirnomental Monitoring and Support Laboratory

EPA -- U. S. Environmental Protection Agency

eV -- electron volts

FAS -- ferrous ammonium sulfate

FC-43 -- perfluorotributylamine

FITOAR -- flame ionization total area

-FP -- free chlorine formation potential at ambient pH and temperature

ft -- foot

GAC -- granular activated carbon

gal -- gallon

gal/min per ft^2 -- gallons per minute per square foot

GC -- gas chromatograph

GC/MS -- gas chromatograph/mass spectrometer

GP -- grob purgeables

GPM -- gallons per minute

HPC -- heterotrophic plate count

hr -- hour

-I -- instantaneous

ID -- inner diameter

in -- inch

infl	-- influent
L	-- liter
lb	-- pound
m	-- meter
mg/l	-- milligram per liter
MID	-- multiple ion detection
min	-- minute
ml	-- milliliter
ml/min	-- milliliters per minute
mm	-- millimeter
ND	-- nondisinfected
ng/l	-- nanogram per liter
$-NH_2Cl$	-- terminal levels after 5-day treatment with chloramine at ambient pH and temperature
NH_2Cl	-- monochloramine
NTU	-- nephelometric turbidity unit
O_3	-- ozone
PNAH	-- polynuclear aromatic hydrocarbons (total)
PRD	-- percent relative deviation
SCFH	-- standard cubic feet per hour
SE	-- solvent extractables
TECC	-- total electron capture concentration
TFIC	-- total flame ionization concentration
THM	-- total trihalomethane
TOC	-- total organic carbon
TOX	-- total organic halogen

ug/l	-- microgram per liter
ul	-- microliter
VOA	-- volatile organics analysis
WCOT	-- wall coated open tubular

METRIC CONVERSION TABLE

ENGLISH UNIT	METRIC EQUIVALENT
1 ft^3	0.02834 m^3
1 ft	30.49 centimeter
1 gal	3.788 liter
1 gpm	3.788 liters/min
1 gal/min per ft^2	40.78 liters/min per m^2
1 in	2.54 cm
mgd	3788 m^3/day
1 lb	453.5 g
1 psi	0.1785 kg/cm^2
1 sq ft	0.0929 m^2

ACKNOWLEDGMENTS

The initial involvement of Noel V. Brodtmann of Environmental Professionals Limited, Metairie, Louisiana and Jack DeMarco of the Cincinnati, Ohio, Water Works in starting this project is greatly appreciated.

The administrative assistance and technical advice of the Project Officer, Ben Lykins, was most valuable in meeting the objectives of this study.

The technical staff of the Jefferson Parish Water Quality Laboratory was instrumental to the success of this project through their long hours of dedicated work. These included Gulser Wood, Robert Grant, Mark Flynn, Joseph Folse, Henry Lala, George Landen, Michelle Lutenbacher, James Massony, Douglas Meadowcroft, Paul O'Rourk, Sushma Pahwa, and Anita Turner. The secretarial services of Marilyn Harding in preparing this report were well performed and appreciated.

Appreciation must also be expressed to Anthony Cosentino and Raymond Hartman for their assistance in maintaining the analytical equipment required to complete this study.

The assistance and cooperation of the plant superintendent, Bill Watson, throughout the course of this study was also appreciated.

SECTION 1

INTRODUCTION

The Mississippi River along with its tributaries drains nearly two-thirds of the Continental United States and supplies a source of drinking water to many cities located along its banks. The waters of the Mississippi River and its tributaries also serve as the receivers for vast quantities of industrial and municipal wastes as well as agricultural run-off, creating various levels of trace organic contamination in this drinking water source. In addition to these trace-level (ng/l) contaminants in the source water, significantly higher levels (ug/l) of organic contamination have been observed to be formed when chlorine is used in the disinfection of potable water. A portion of this research project, which was jointly funded by the USEPA and Jefferson Parish, was to determine which of the alternative disinfectants (ozone, chlorine dioxide, chloramine, and chlorine), when used in conjunction with granular activated carbon filtration, would minimize these levels of trace organic contaminants while providing a bacteriologically acceptable drinking water. In view of a previous report[1] that has indicated that pilot columns were quite effective in predicting full-scale plant operation, an extensive pilot column system was developed for this evaluation.

The objectives of this research program were to investigate the chemical, bacteriological, and health effects of the alternative disinfectants in conjunction with granular activated carbon filtration as follows:

1. To provide an operational pilot column system for the collection of water samples for health effects toxicological testing.
2. To characterize the chemical and bacteriological effects of the alternative disinfectants on the dissolved organic contaminant levels in drinking water.
3. To evaluate the chemical and bacteriological

effects of predisinfection and granular activated carbon filtration on drinking water quality as compared to sand filtration.

4. To evaluate the effects of post disinfection with monochloramine and free chlorine following granular activated carbon filtration relative to the formation of total organic halides and trihalomethanes.

The health effects toxicological testing was conducted by the USEPA Health Effects Research Laboratory and involved such tests as the Ames Salmonella Assay, a Subchronic in Vivo Toxicity in Mice, the Sencar Mouse Skin Initiation/Promotion Assay, A Rat Liver Foci Assay, and the Lung Adenoma Assay in Strain A Mice. In this study, drinking water from various disinfected process streams was concentrated 400 times by reverse osmosis and 4000 times by macroreticular resin adsorption. A complete report of the results of the toxicological testing, entitled "Results of Toxicological Testing of Jefferson Parish Pilot Plant Samples" was presented in the proceedings of the Second International Symposium on Health Effects of Drinking Water Disinfectants and Disinfection By-Products in August 1985 and will be published in Environmental Health Perspectives.

This report contains a complete description of each process stream of the pilot column system used during the operational period from May 1983 through May 1984. A thorough description of the analytical program used in monitoring the various parameters of interest is presented along with a thorough discussion of each individual parameter relative to the project objectives. This is followed by a brief summary of the overall effects of the alternative disinfectants and granular activated carbon filtration on the levels of organic contaminants in drinking water.

SECTION 2

CONCLUSIONS

1. The best pretreatment for minimizing organic contaminants was ozonation, with the next best pretreatment being no pretreatment at all. Ozonation produced reductions of all parameters monitored except for the volatile organics. Only a minimum formation of disinfection by-products were observed for ozonation, specifically alkylaldehydes. However, it is unlikely that all of the ozonation by-products were observed, since the extraction methology used was not suitable for the recovery of the more water soluble oxygenated by-products.

2. Predisinfection with chlorine dioxide resulted in some increase in TOX, total alkylbenzene, and total electron capture concentration but no increase in the level of THMs was observed. Also, essentially no reductions of the organic contaminants present in the nondisinfected influent were observed for chlorine dioxide.

3. The extent of by-product formation through pretreatment with chloramines was determined by the extent of free chlorine contact with precursor material,(i.e., premixed chloramines produced significantly lower levels of by-product formation than did chloramines formed in the process stream). The levels of by-products formed by premixed chloramines were similiar to those formed by chlorine dioxide. Essentially no reductions of organic contaminants present in the nondisinfected influent were observed for chloramines.

4. Predisinfection with chlorine produced the greatest amount of disinfection by-products along with essentially no removal of those organic contaminants present in the nondisinfected influent. The greatest increases were observed for the trihalomethanes, TOX, total electron capture concentration, and total flame ionization concentration. Numerous increases of both identified and unidentified nonhalogenated by-products as well as halogenated by-products were observed.

5. Though the heterotrophic plate counts in the effluent of all of the GAC columns in each process stream were similiar to

each other as well as to that of the nondisinfected influent, the heterotrophic plate counts in the effluent of the ozone sand column were roughly ten times that of the nondisinfected sand column and twenty times that of the other disinfected sand columns, indicating a biologically activated ozone sand column. Significant biological degradation of TOC averaging 0.5 mg/l was observed across the ozone sand column along with some additional reductions of total flame ionization concentration, total electron capture concentration, and triphenylmethane. Indications were that the majority of the biological degradation occurred for nonsynthetic organic substances.

6. Though sand filtration had little relative effect upon the dissolved organic content of the chlorine dioxide and chloramine process streams, significant reductions of total flame ionization concentration, total alkylbenzene, total phthalate, and total chlorobenzene were observed across the chlorine sand column. However, the effluent levels of these parameters remained considerably higher than those of the other process streams. In addition, the level of THMs increased an average of 16 ug/l across the chlorine sand column because of the additional chlorine contact time.

7. In general, predisinfection had relatively little significant effect on the removal of dissolved organic contaminants by GAC filtration. Somewhat better reductions of TOC and TOX were observed for the ozone GAC columns, whereas somewhat poorer reductions of TOX, total electron capture concentration, THMs, and 1,2-dichloroethane were observed for the chlorine GAC columns.

8. Formation potential studies after sand and GAC filtration comparing chlorine and chloramines indicated that post chlorination produced significantly greater levels of TOX and THMs than did post chloramination.

9. A significantly greater level of TOX than that of the THMs was produced in the chloramine process stream after a brief 9 second contact of nondisinfected influent water with free chlorine before the conversion of free chlorine to chloramines. This indicated that lower Mississippi River water contained TOX precursors that were much more reactive than the precursors of the THMs.

10. Variations in the effectiveness of several different types of GAC relative to the removal of dissolved organic contaminants were indicated in the GAC selection study, with the greater variations occurring for the low-molecular-weight organic substances (e.g., the THMs and 1,2-dichloroethane).

SECTION 3

RECOMMENDATIONS

1. Further studies should be conducted to identify the ozonation by-products of both individual compounds and multiple component mixtures. This will require the development of more diverse recovery and analytical methology.

2. Concurrent health risk assessments are needed to determine the significance of newly identified disinfection by-products.

3. A more thorough evaluation of postdisinfection following GAC filtration that closely simulates normal treatment plant operation should be conducted to more accurately determine the effects of chlorine and chloramines on the final product water reaching the consumer.

4. Further studies should be developed to identify those TOX by-products other than the THMs that are formed during chlorination, particularly those whose precursors have higher reaction rates than those of the THMs.

5. A pilot-scale simulation of normal treatment plant operation should also be conducted to evaluate the overall chemical and biological effects of preformed chloramines on water quality versus those of chloramines formed within the water treatment process stream. While preformed chloramines produce lower TOX levels, there is some question as to their effectiveness as a disinfectant.

SECTION 4

PILOT COLUMN CONFIGURATION

The raw water intake of East Jefferson Parish is located on the east bank of the Mississippi River at river mile 105.4 above the mouth of the river. At this site raw water is pumped to four separate treatment plants. Nondisinfected clarified water was supplied to the pilot column system by the Permutit III plant as indicated in Figure 1 which depicts the general configuration of the pilot column system.

Raw river water was clarified with diallyldimethylammonium chloride and/or dimethylamine type cationic polymers and fluoridated with fluosilicic acid before entering the pilot column system. At this point the clarified water was filtered through one of two pressure sand filters and divided into five process streams. A detailed description of each disinfected process stream within the pilot column system is presented in Figure 2.

Each disinfected process stream consisted of a thirty minute disinfectant contact chamber followed by parallel filtration through a sand column, a granular activated carbon (GAC) column, and a duplicate granular activated carbon column. The duplicate column was used to determine variability between GAC columns within the same process stream. The configuration of the nondisinfected process stream was identical to that of the disinfected process streams except that the disinfectant contact chamber was eliminated.

All materials used in the construction of the pilot column system including all pumps, pressure sand filters, plumbing, contact chambers, and columns were composed of stainless steel, teflon, or glass. Plastic flow totalizers were installed at the ends of each process stream, however, all samples were taken upstream of these totalizers as indicated. Each pilot column was constructed from 6 in. I.D. x 10 ft. glass pipe with 150 lb. stainless steel blind flange ends and a teflon/stainless steel screen underdrain which is shown in Figure 3. The pilot columns were charged with 6.8 ft. of either sand or GAC media to obtain a 20 minute empty bed contact time (EBCT) with a flow of 0.5 GPM.

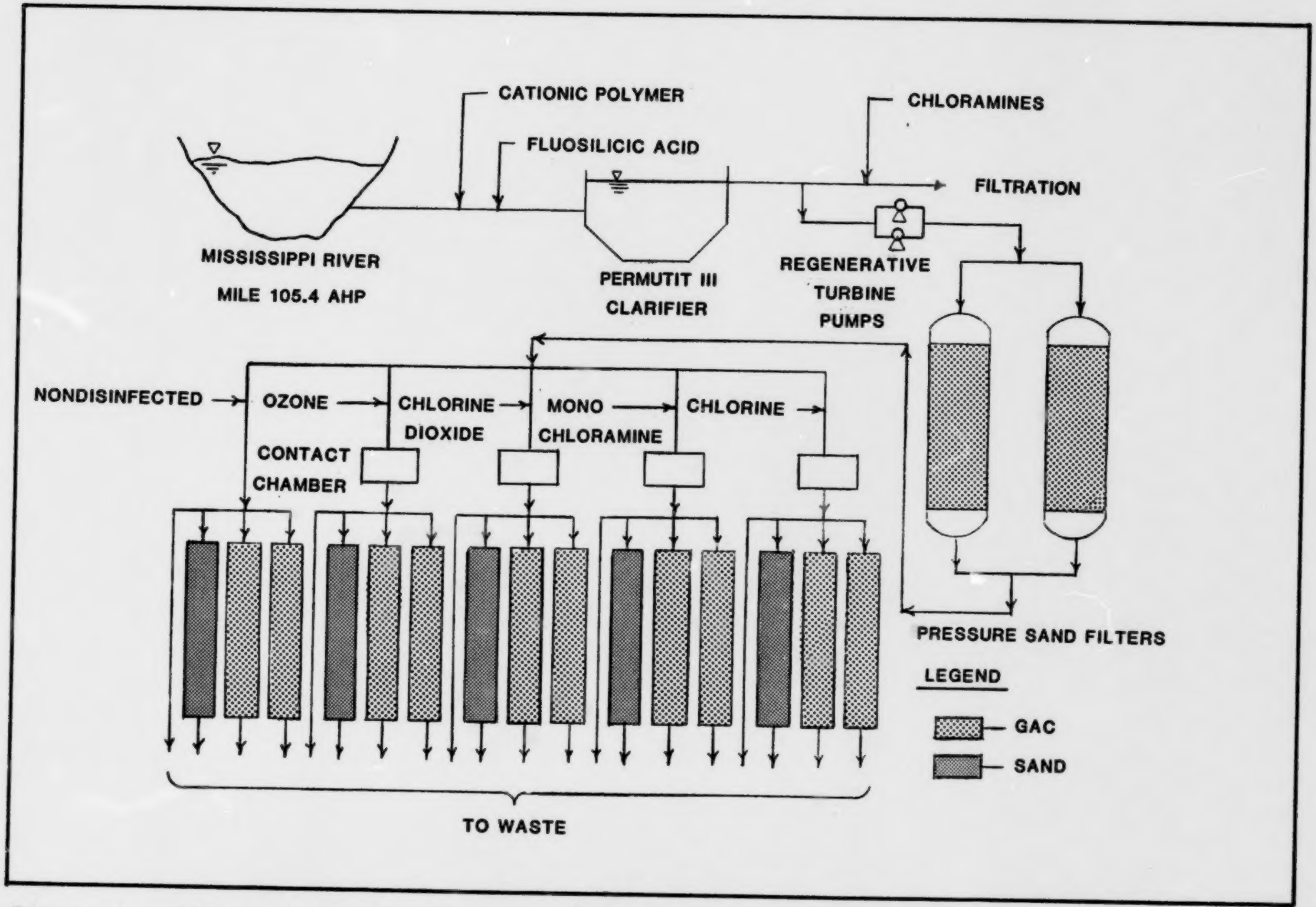

CATIONIC POLYMER
FLUOSILICIC ACID
CHLORAMINES
FILTRATION
MISSISSIPPI RIVER
MILE 105.4 AHP
PERMUTIT III
CLARIFIER
REGENERATIVE
TURBINE
PUMPS
NONDISINFECTED
OZONE
CHLORINE
DIOXIDE
MONO
CHLORAMINE
CHLORINE
CONTACT
CHAMBER
PRESSURE SAND FILTERS
LEGEND
GAC
SAND
TO WASTE

Figure 1. Pilot Column System Flow Schematic.

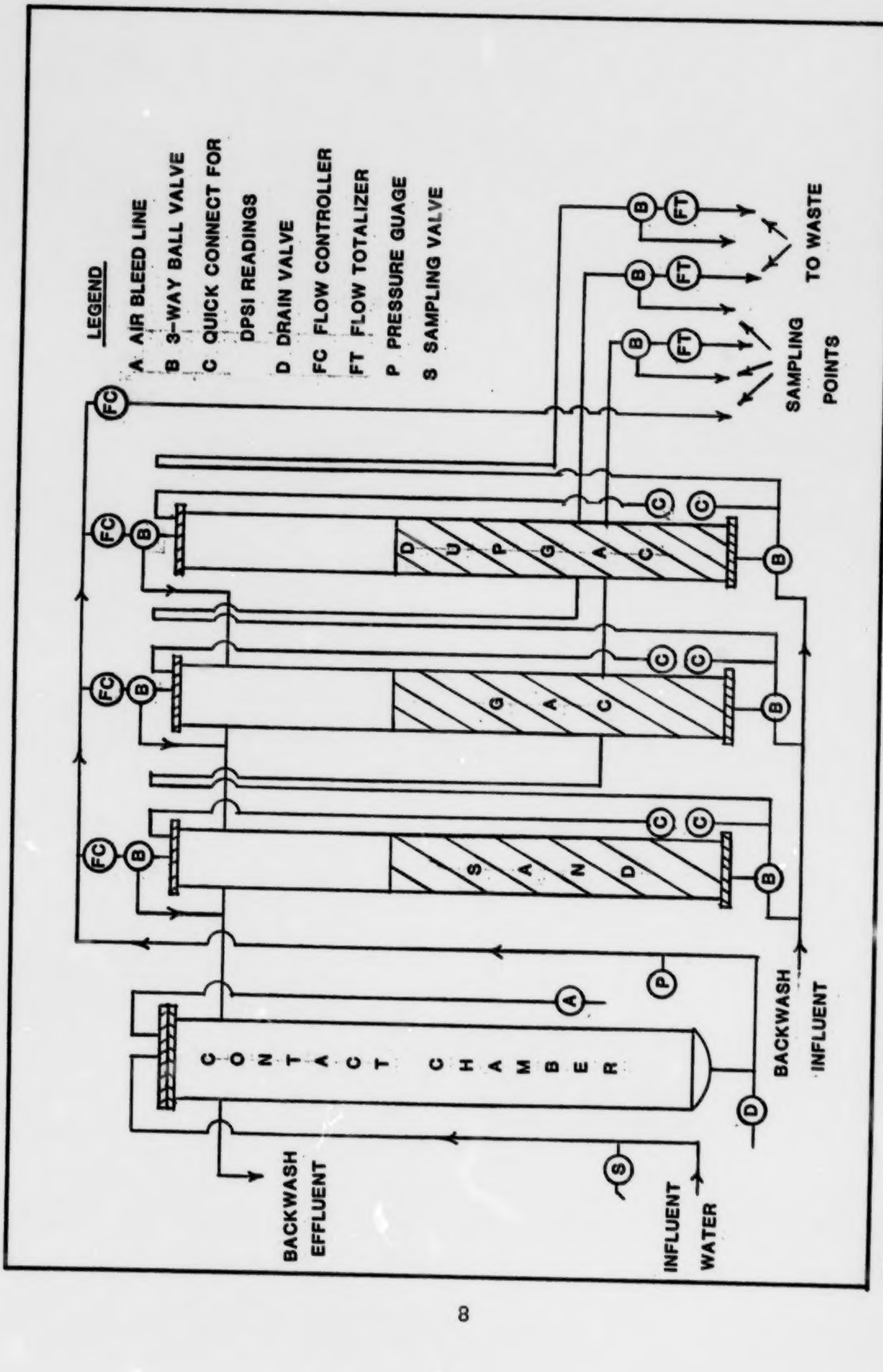

LEGEND
A AIR BLEED LINE
B 3-WAY BALL VALVE
C QUICK CONNECT FOR DPSI READINGS
D DRAIN VALVE
FC FLOW CONTROLLER
FT FLOW TOTALIZER
P PRESSURE GUAGE
S SAMPLING VALVE
CONTACT CHAMBER
SAND
GAC
DUPGAC
BACKWASH EFFLUENT
INFLUENT WATER
BACKWASH INFLUENT
SAMPLING POINTS
TO WASTE
FC
B
C
FT
A
P
D
S

Figure 2. Detailed Schematic of Each Disinfectant Process Stream.

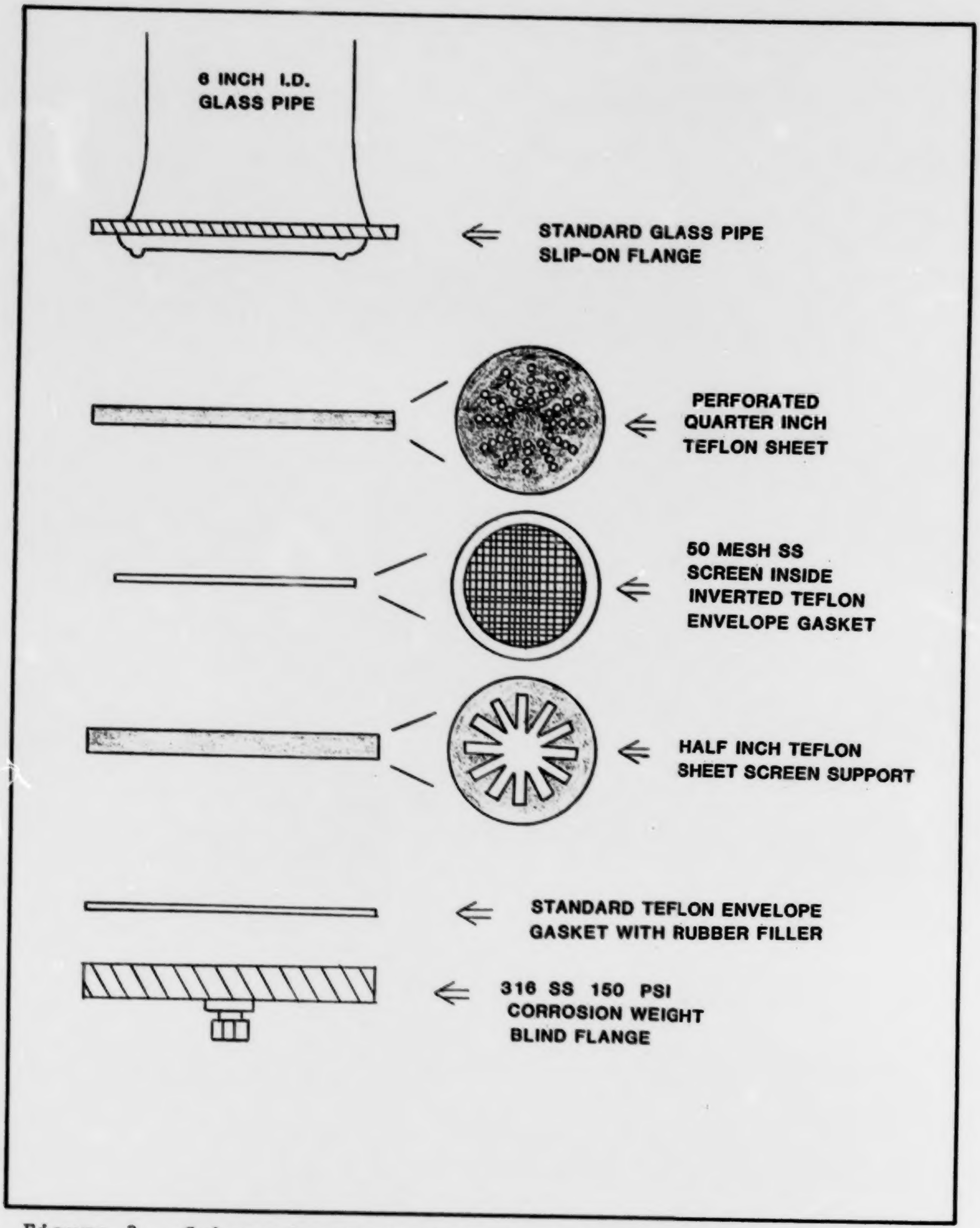

6 INCH I.D.
GLASS PIPE
STANDARD GLASS PIPE
SLIP-ON FLANGE
PERFORATED
QUARTER INCH
TEFLON SHEET
50 MESH SS
SCREEN INSIDE
INVERTED TEFLON
ENVELOPE GASKET
HALF INCH TEFLON
SHEET SCREEN SUPPORT
STANDARD TEFLON ENVELOPE
GASKET WITH RUBBER FILLER
316 SS 150 PSI
CORROSION WEIGHT
BLIND FLANGE

Figure 3. Schematic of the Underdrain System For Each Pilot Column.

Each disinfectant contact chamber was constructed from 12.75 in. O.D. (0.18 in. wall) stainless steel pipe with stainless steel blind flanged or capped ends. The chlorine dioxide, chloramine, and chlorine contact chambers were 10 ft. in height in order to produce thirty minutes of disinfectant contact time with a flow of 2 GPM. The ozone contact chamber was 11 ft. in height and designed for countercurrent operation with the water entering at the top of the contact chamber and the ozone gas stream entering on the bottom as indicated in Figure 4. The water and ozone gas influent lines were oriented such that the influent water would be in contact with the ozone gas stream for thirty minutes. Ozone gas exiting the contact chamber was reduced by passage through a pelletized nickel oxide column which was heated to prevent condensation.

Ozone was generated from compressed dry air using an electrically powered ozone generator with a maximum output capacity of 0.25 lb/day. Chlorine dioxide was generated using two solutions, one containing sodium chlorite and sodium hypochlorite and the other containing sulfuric acid. A 50 percent excess of sulfuric acid was added to adjust the pH of the final solution to 4 which is the pH of optimum chlorine dioxide yeild as recommended by White[2]. These two solutions were pumped together and received in-line mixing in a small generating tower constructed of teflon shavings and glass. All components which came into contact with chlorine dioxide were made of teflon or glass. A 96 percent yeild of chlorine dioxide was observed for this method of generation. Chlorine gas was fed to both the chloramine and chlorine process streams using teflon eductors. Ammonia was added to the chloramine process stream in the form of an ammonium hydroxide solution which was pumped into the process stream ahead of the chlorine eductor. During the latter part of the operational period it was noticed that somewhat higher total organic halide (TOX) and trihalomethane (THM) levels had been observed for the chloramine process stream than for the finished water of the Permutit III treatment plant which also used chloramine disinfection. These higher concentrations were traced back to the ammonium hydroxide pump which operated on a 9 second pulsed cycle and thus allowed a portion of the influent water to come into contact with free chlorine for a very short period. This short contact of precursor material with free chlorine caused the formation of TOX and THMs thus increasing their concentrations. No increase in concentration was observed in the Permutit III treatment plant as ammonia was added continuously in the form of anhydrous ammonia gas. A more detailed evaluation of the effect of this short contact with free chlorine will be present in later sections of this report covering TOX and THMs.

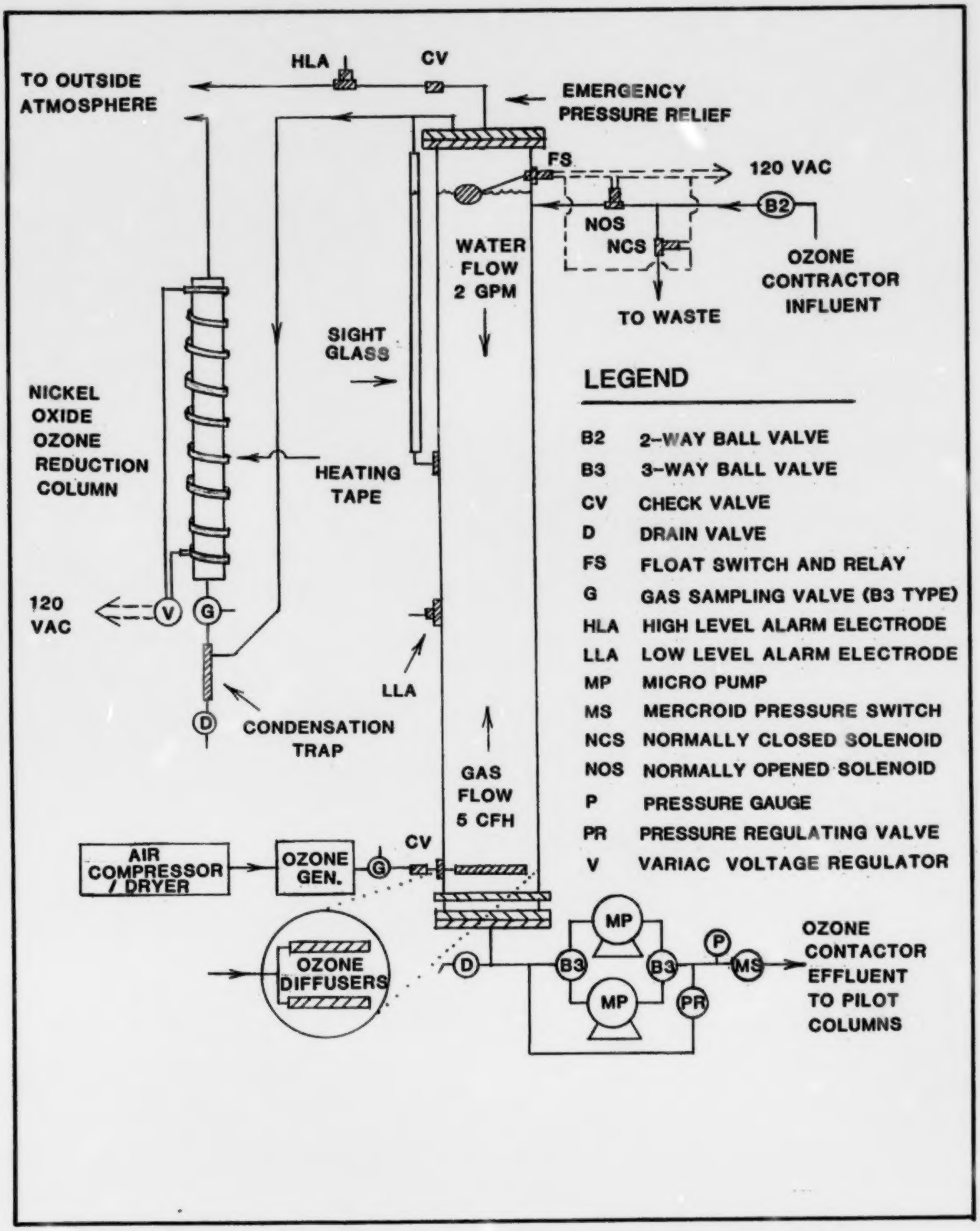

HLA
CV
TO OUTSIDE ATMOSPHERE
EMERGENCY PRESSURE RELIEF
FS
120 VAC
B2
NOS
NCS
OZONE CONTRACTOR INFLUENT
TO WASTE
WATER FLOW 2 GPM
SIGHT GLASS
NICKEL OXIDE OZONE REDUCTION COLUMN
HEATING TAPE
120 VAC
V
G
LLA
CONDENSATION TRAP
D
GAS FLOW 5 CFH
AIR COMPRESSOR / DRYER
OZONE GEN.
G
CV
OZONE DIFFUSERS
D
MP
B3
B3
MP
P
PR
MS
OZONE CONTACTOR EFFLUENT TO PILOT COLUMNS
LEGEND
B2 2-WAY BALL VALVE
B3 3-WAY BALL VALVE
CV CHECK VALVE
D DRAIN VALVE
FS FLOAT SWITCH AND RELAY
G GAS SAMPLING VALVE (B3 TYPE)
HLA HIGH LEVEL ALARM ELECTRODE
LLA LOW LEVEL ALARM ELECTRODE
MP MICRO PUMP
MS MERCROID PRESSURE SWITCH
NCS NORMALLY CLOSED SOLENOID
NOS NORMALLY OPENED SOLENOID
P PRESSURE GAUGE
PR PRESSURE REGULATING VALVE
V VARIAC VOLTAGE REGULATOR

Figure 4. Detailed Schematic of the Ozone Contact Chamber.

SECTION 5

SAMPLING, ANALYSIS, AND QUALITY ASSURANCE

SAMPLING, PRESERVATION, AND STORAGE

The sampling and analysis schedule for the pilot column system during the first year of operation is presented in Table 1. The location of the sampling points corresponding to the numbers listed across the top of Table 1 are shown in Figure 5. Those chemical analyses which were performed included total organic carbon (TOC), total organic halide (TOX), volatile organics (VOA), capillary gas chromatography (CGC) of solvent extractables with electron capture and flame ionization detection, gas chromatography/mass spectrometry (GC/MS) of both closed loop purgeables and solvent extractables, ozone, chlorine dioxide, chloramine, free chlorine, pH, and temperature. Those volatile and solvent extractable organics monitored during this study are listed in Tables 2, 3, and 4 along with their detection limits and, where applicable, their percent recoveries. The bacteriological parameters monitored included heterotrophic plate count, dissolved oxygen, Analytab API speciation, and total coliform. Quantitative grob purgeables analysis using CGC was also attempted, however, the reproducibility of the method used in conjunction with the low concentrations present was not sufficient for quantitation. This procedure was, however, useful for qualitative confirmation of volatile organics using capillary column GC/MS and was used for this purpose beginning on day 10 of the operational period. Those sampling locations in Figure 5 designated 22-37 were formation potential samples which were performed in the laboratory. The free chlorine formation potential samples ($-CL_2$) were dosed with varying amounts of free chlorine depending upon their demand and stored for five days at 28°C. All disinfected influents and all sand column effluents were dosed with 4 mg/l Cl_2 while the nondisinfected influent was dosed with 7 mg/l Cl_2. All chloramine formation potential samples ($-NH_2Cl$) were dosed with 5 mg/l ammonia-nitrogen followed by 4 mg/l Cl_2 and stored at 28°C for five days. After the five day storage period had elapsed, all formation potential samples were dechlorinated with either sodium thiosulfate or sodium sulfite.

TABLE 1. PILOT COLUMN SYSTEM SAMPLING AND ANALYSIS SCHEDULE

TYPE OF ANALYSIS	NO. PER WEEK	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37
TOC	21	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W																
TOX-I	10-1/2	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B																
TOX-NH_2Cl	7-1/2	B	B	B	B	B	B										B							B		B		B		B		B		B		B		B
TOX-Cl_2	7-1/2	B	B	B	B	B	B													B			B		B		B		B		B		B		B		B	
VOA-I	21	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W																
VOA-NH_2Cl	15	W	W	W	W	W	W										W							W		W		W		W		W		W		W		W
VOA-Cl_2	15	W	W	W	W	W	W													W			W		W		W		W		W		W		W		W	
CGC-SE	18	B	W	W	W	W	W	B	W	W	B	W	W	B	W	W	B	W	W	B	W	W																
CGC-CHI	8	B	B	B	B	B	B	B		C		B		C		B		C		B		C																
GC/MS-GP	5		W	W	W	W	W																															
GC/MS-SE	5		W	W	W	W	W																															
GC/MS-CHI	1/2		B																																			
TOTAL BACTERIA	81	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	W	T	T	W	T	T	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W
TOTAL COLIFORM	81	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	W	T	T	W	T	T	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W
API-SPECIATION	30	W	W	W	W	W		W	W	W	W	W	W	W	W	W	B	W	W	B	W	W	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B
DISSOLVED OXYGEN	40				X	X	X	X	X	X	X	X	X	X	X	X	X	X		X	X		X	X														
DISINF. RESID.	88		D	D	D	D					F	F	F	F	F	F	F	F	F	F	F	F																

W - 1/week	B - biweekly	-I: instantaneous	-SE: solvent extractables
T - 3/week	C - biweekly composite	-NH_2Cl: chloramine formation potential	-CHI: chlorinated hydrocarbon insecticides
F - 5/week	D - daily	-Cl_2: freechlorine formation potential	-GP: grob purgeables
X - 2/week			

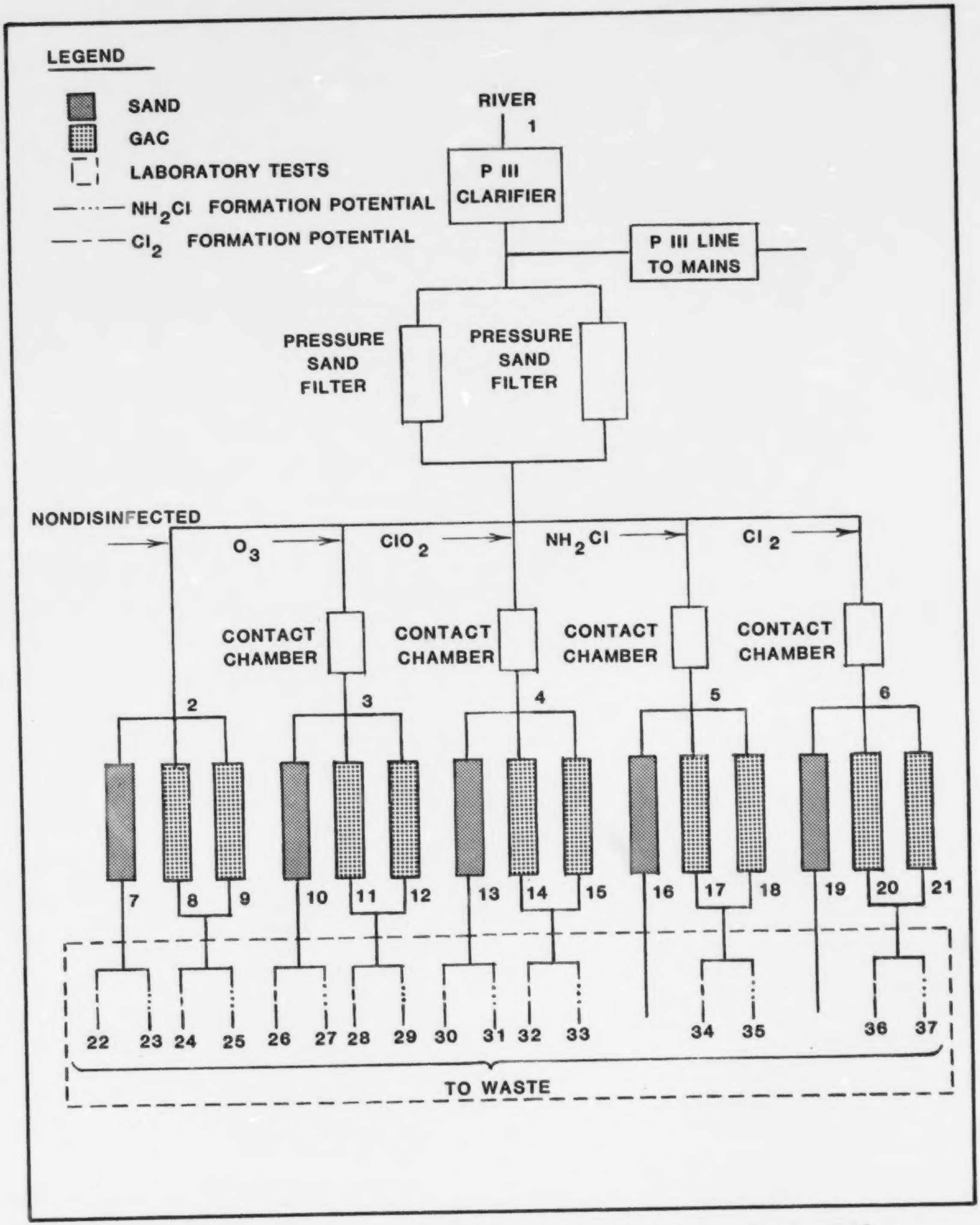

LEGEND
SAND
GAC
LABORATORY TESTS
NH2Cl FORMATION POTENTIAL
Cl2 FORMATION POTENTIAL
RIVER
1
P III CLARIFIER
P III LINE TO MAINS
PRESSURE SAND FILTER
PRESSURE SAND FILTER
NONDISINFECTED
O3
ClO2
NH2Cl
Cl2
CONTACT CHAMBER
CONTACT CHAMBER
CONTACT CHAMBER
CONTACT CHAMBER
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
TO WASTE

Figure 5. Schematic of the Sampling Locations of the Pilot Column System.

TABLE 2. GAS CHROMATOGRAPHY STANDARD CONCENTRATIONS AND DETECTION LIMITS FOR VOLATILE ORGANICS ANALYSIS.

COMPOUND	STANDARD CONC. (ug/l)	METHOD* DETECTION LIMIT (ug/l)
1,2-dichloroethylene	5.0	0.050
dichloromethane	2.1	0.030
tetrachloromethane	2.6	0.035
chloroform	2.4	0.005
1,1,2-trichloroethylene	3.5	0.020
bromodichloromethane	3.2	0.040
1,2-dichloroethane	3.0	0.030
dibromochloroethane	5.9	0.060
1,1,2-trichloroethane	2.3	0.020
bromoform	11.6	0.040

---

* Measured at 2x noise level.

TABLE 3. GAS CHROMATOGRAPHY STANDARD CONCENTRATIONS, DETECTION LIMITS, AND PERCENT RECOVERIES FOR SOLVENT EXTRACTABLE HYDROCARBON ANALYSIS.

COMPOUND	STANDARD CONC (mg/l)	PENTANE EXTRACTION RECOVERY (%)	METHOD* DETECTION LIMIT (ng/l)
ethylbenzene	1.06	68.3	0.42
m-& p-xylene	1.04	67.7	0.35
o-xylene	0.99	73.0	0.40
cumene	1.03	68.0	0.51
3-ethyltoluene	1.00	68.5	0.42
4-ethyltoluene	1.03	64.1	0.41
1,3,5-trimethylbenzene	1.01	75.5	0.38
2-ethyltoluene	1.02	70.1	0.41
1,2,4-trimethylbenzene	1.00	75.8	0.38
decane	0.99	28.6	1.08
1,3-dichlorobenzene	1.51	75.5	0.72
octanal	1.50	75.6	0.57
1,4-dichlorobenzene	1.50	74.6	0.68
1,2,3-trimethylbenzene	0.94	75.3	0.39
p-cymene	1.01	69.2	0.43

---

*Measured at 2x noise level with percent recoveries applied.

TABLE 3. (Cont.)

COMPOUND	STANDARD CONC (mg/l)	PENTANE EXTRACTION RECOVERY (%)	METHOD* DETECTION LIMIT (ng/l)
1,2-dichlorobenzene	1.50	77.0	0.70
indene	0.93	77.9	0.45
1,3-diethylbenzene	1.23	70.0	0.43
1,4-diethylbenzene	0.75	68.3	0.44
nitrobenzene	1.02	36.3	1.21
d-fenchone	1.43	77.8	0.45
undecane	1.01	30.3	1.02
nonanal	1.45	77.9	0.53
1,2,4,5-tetramethylbenzene	1.02	76.1	0.35
1,2,3,5-tetramethylbenzene	0.89	75.9	0.37
1,2,3,4-tetramethylbenzene	0.94	78.5	0.38
tetralin	1.62	78.8	0.81
2-nitrotoluene	0.97	78.0	0.28
1,2,4-trichlorobenzene	1.49	80.2	0.84
naphthalene	1.05	80.2	0.32
dodecane	0.98	31.8	0.94
1-chloro-4-nitrobenzene	3.02	71.6	0.89
1-chloro-2-nitrobenzene	2.91	64.8	0.93
2-methylnaphthalene	2.07	81.3	0.36
1-methylnaphthalene	0.99	81.6	0.34
cyclohexylbenzene	1.04	77.4	0.37
biphenyl	1.02	81.6	0.34
2-ethylnaphthalene	1.98	80.3	0.35
2,6-dimethylnaphthalene	0.98	82.4	0.33
2,3-dimethylnaphthalene	1.06	82.7	0.34
1,2-dimethylnaphthalene	3.03	82.0	0.70
acenaphthene	1.02	82.3	0.32
pentadecane	1.08	47.4	0.63
2,4-dinitrotoluene	3.02	30.9	2.35
fluorene	0.99	85.3	0.34
hexadecane	1.08	56.3	0.53
diethylphthalate	3.05	69.1	0.75
tributylphosphate	1.97	18.8	3.14
heptadecane	1.03	67.1	0.48
4-nonylphenol	1.03	80.6	3.30
atrazine	4.07	15.1	6.16
dipropylphthalate	2.61	81.6	0.63
phenanthrene	1.99	86.8	0.36
anthracene	1.59	84.0	0.39
diisobutylphthalate	2.09	83.0	0.61

---

*Measured at 2x noise level with percent recoveries applied.

TABLE 3. (Cont.)

COMPOUND	STANDARD CONC (mg/l)	PENTANE EXTRACTION RECOVERY (%)	METHOD* DETECTION LIMIT (ng/l)
nonadecane	1.13	71.9	0.49
alachlor	2.52	66.9	0.85
dibutylphthalate	1.97	82.3	0.64
eicosane	1.16	73.0	0.49
triphenylmethane	1.68	85.9	0.37
fluoranthene	1.99	84.8	0.40
pyrene	2.07	83.9	0.43
1,2-butylbenzylphthalate	2.56	75.8	0.74
bis-[2-ethylhexyl]phthalate	2.02	81.9	0.65
dioctylphthalate	2.02	79.1	0.76

---

*Measured at 2x noise level with percent recoveries applied.

TABLE 4. GAS CHROMATOGRAPHY STANDARD CONCENTRATIONS, DETECTION LIMITS, AND PERCENT RECOVERIES FOR CHLORINATED HYDROCARBON INSECTICIDE ANALYSIS.

COMPOUND	STANDARD CONC (mg/l)	PENTANE EXTRACTION RECOVERY (%)	METHOD* DETECTION LIMIT (ng/l)
α-BHC	0.025	89.5	0.004
hexachlorobenzene	0.026	85.4	0.005
β-BHC	0.100	91.6	0.059
γ-BHC	0.025	91.9	0.007
pentachloronitrobenzene	0.040	93.2	0.006
heptachlor	0.025	90.7	0.015
α-chlordene	0.039	90.2	0.010
aldrin	0.050	86.0	0.005
γ-chlordene	0.100	89.9	0.013
β-chlordene	0.100	90.6	0.012
DCPA	0.100	94.1	0.013
heptachlorepoxide	0.08	90.4	0.010
oxy-chlordane	0.100	96.8	0.012
γ-chlordane	0.075	89.8	0.006
o,p'-DDE	0.099	91.2	0.009
α-chlordane	0.080	97.0	0.005
dieldrin	0.120	89.4	0.013
p,p'-DDE	0.100	94.0	0.005
o,p'-DDD	0.200	90.9	0.018

---

*Measured at 2x noise level with percent recoveries applied.

TABLE 4. (Cont.)

COMPOUND	STANDARD CONC (mg/l)	PENTANE EXTRACTION RECOVERY (%)	METHOD* DETECTION LIMIT (ng/l)
endrin	0.200	89.9	0.021
endosulfan II	0.199	88.8	0.009
m,p'-DDD	0.298	92.6	0.018
perthane	5.030	95.5	0.135
p,p'-DDD	0.190	83.8	0.016
o,p'-DDT	0.225	96.0	0.029
p,p'-DDT	0.260	98.4	0.028

*Measured at 2x noise level with percent recoveries applied.

The sample containers used during this study were various sized amber glass bottles with teflon lid liners except for those used for microbiological sample collection which were appropriately sized auto clavable plastic bottles. Each sample bottle was labeled prior to sampling with the code for a specific sampling point. All bottles and lid liners that were used for inorganic sampling were washed with mild detergent, rinsed with dilute hydrochloric and nitric acid solutions, rinsed 2-3 times with deionized water, and oven dried at 130°C. All bottles and lid liners used for organic sampling were washed with mild detergent, rinsed with tap water followed by deionized water, rinsed with acetone, and oven dried at 180°C. All microbiological sampling bottles were detergent washed, rinsed, and autoclaved at 121°C for minimum of 15 minute.

All samples collected for this study were grab samples. All sample bottles not containing preservatives or dechlorinating agents were rinsed with sample prior to sample collection. All organic samples were collected head-space free. Dissolved oxygen, temperature, and disinfectant residuals were determined on-site. Sodium sulfite (5 mg/l) was used as the dechlorinating agent for TOX samples. Samples for all other analyses were not chemically preserved. All samples that were not analyzed on the same day as collected were stored at 4°C until analyzed. Samples for all analysis not performed on site were collected in duplicate. The duplicate sample was analyzed when the original sample analysis result was suspected of being contaminated as determined by the section analyst, i.e. data obtained did not conform to the prevailing trend.

ANALYTICAL PROCEDURES

Total Organic Carbon (TOC) --

Total organic carbon was analyzed using EMSL Method 415.2 with the exceptions that the samples were stored at 4°C without acidification and a linearity chec(2,5 & 10 mg/l standards) was performed on a weekly basis.

Total Organic Halide (TOX) --

Total organic halide analyses were performed using EMSL Method 450.1.

Volatile Organics Analysis (VOA) --

For volatile organics analysis EMSL Method 501.1 was used with the following exceptions:

1. A 12 ft. Durapak n-Octane/Porasil C column was used with He flow of 25 ml/min and was programed from 50-150°C at 4°/min with a 2 minutes hold at 50°C.
2. A Tenax trap was used with a He purge flow of 20 ml/min and a desorption time of 5 minutes.
3. One standard was analyzed per 8 hr. shift which was prepared headspace free in a 1 liter bottle.
4. 1,1,2,2-Tetrachloroethane was used as the internal standard.

The volatile organic detection limits observed for this method are presented in Table 2 as previously indicated.

Closed Loop Purgeables --

The method used for analyzing closed loop purgeables via closed loop stripping was that described by W. E. Coleman et al.[3] except that the water bath temperature was held constant at 40°C, the temperature of the trap was held at 50°C, the sample volume used was 1 liter, and the purging time was 2 hours. The closed loop stripping equipment used was a Brechbuhler AG.

Solvent Extractable Hydrocarbons and Chlorinated Hydrocarbon Insecticides --

The following in-house procedure was designed to isolate those organic compounds which are solvent extractable from a neutral water sample and amenable to analysis by gas chromatography, and to prevent the contamination of laboratory air with chlorinated solvent (methylene chloride) which affects both TOX and VOA analyses.

Because of the low concentrations of organic contaminants in the lower Mississippi River water, 6 liter samples had to be extracted to detect the trace levels of organics present. For this reason, special order 7.5 liter separatory funnels with teflon stopcocks and stoppers were obtained and separatory funnel holders were constructed for the extraction process using mechanical shakers.

All glassware was cleaned with soap and water, acetone rinsed, and, except for the 7.5 liter separatory funnels, heated overnight in a 180°C drying oven. Grab water samples were collected in two 1 gallon amber bottles, stored at 4°C, and warmed to 20°C before extraction. After shaking the sample to ensure homogenity, six liters of sample was transferred into a 7.5 liter separatory funnel using a 1 liter graduated cylinder. The sample was then spiked with 20 ul of an internal standard solution containing 1-chloroalkanes (C_5, C_6, C_7, C_8, C_{10}, C_{12}, C_{14}, C_{16}, & C_{18}) and Endosulfan I in acetone. The sample was then serially extracted with 50, 50, and 50 ml of resi-analyzed pentane. During each extraction, the sample was shaken for 10 minutes on a mechanical shaker and the pentane layer, including any emulsion, collected in a receiving flask. When the extraction was completed, the aqueous layer was discarded. Emulsions were broken by high speed centrifugation in screw top centrifuge tubes with teflon lined caps. The use of pre-extracted sodium sulfate for removing water from the extract was not warranted or desired as it introduced a considerable amount of background contamination which in many instances was greater than the level of organic contaminants being monitored.

Following centrifugation, the extract was decanted with pentane rinses into a 500 ml Kuderna-Danish apparatus with a 10 ml calibrated receiver to which a few grains of pre-extracted sand had previously been added to reduce the possibility of bumping during the boil down. The extract was brought to a very low boil on a steam bath and reduced to a volume of approximately 10 ml using a three ball macro Snyder condenser. At this point 0.5 ml of resi-analyzed hexane was added to the extract in order to reduce the evaporation loss of the final extract. The 10 ml receiver was then fitted with a three ball micro Snyder condenser and the extract volume was reduced to 0.5 ml using a low temperature tube heater. The extract volume was then further reduced to a final volume of 0.3 ml with a dry air stream and the extract was split into two 0.15 ml portions and placed into two 0.2 ml microvials with teflon lined caps using a prerinsed disposable pipette. The microvials were than stored in a refrigerator for subsequent analysis by GC using flame ionization and electron capture detection and by GC/MS.

Analysis by gas chromatography was performed using a one minute splitless injection of 2 ul of extract onto a 50 m x 0.25 mm I.D. Durabond DB-5 WCOT fused silica capillary column. The column temperature program was 15 minutes isothermal at 40°C followed by a temperature ramp at 3°C/min to an upper temperature limit of 260°C. The linear gas velocity of the helium carrier gas was 25 cm/sec at 260°C.

The detection limits and percent recoveries of this analytical method which produced a concentration factor of 15,000, are presented in Tables 3 and 4 as previously indicated.

Confirmation of Volatile and Nonvolatile Organics by GC/MS --

Qualative analysis was performed on those organic substances isolated via Grob and solvent extraction techniques with a Finnigan Model 4023 Gas Chromatograph/Mass Spectrometer/Data System. The Grob analysis was used to confirm all volatile components. Complete mass spectra were recorded from 45-260 AMU for the Grob analyses and from 45-450 AMU for the solvent extractable hydrocarbon analyses. Solvent extractable pesticides were analyzed using the more sensitive multiple ion detection (MID) technique. The ions monitored in the MID analyses were generally those reported in the Federal Register. However, in some instances other ions were monitored because of interferences. A 4 msec hold at low mass and a scan cycle of 1 sec was used with all spectra recorded at 70 eV. The gas chromatographic column used for all analyses was a 50 m x 0.25 mm I.D. Durabond DB-5 WCOT fused silica capillary column having a linear gas velocity of 25 cm/sec at 260°C with helium as the carrier gas. The oven of the gas chromatograph was held at 40°C for 15 min and then programed at 3°C/min to 300°C. The system was operated with the capillary column connected directly to the source with a transfer zone temperature of 250°C. Archival storage on 9 track magnetic tape was used for all raw and finished data.

GC/MS system performance was checked on a weekly basis by injection of a system performance standard which contained 500 mg/l of each of the following constituents: decafluorotriphenylphosphine (DFTPP), 2-octanone, decane, 1-octanol, undecane, 2,6-dimethylphenol, 2,6-dimethylaniline, dodecane, naphthalene, tridecene, and tridecane. The tune on the instrument was evaluated by analyzing the mass spectra of chromatographed DFTPP with respect to the criteria described in the Federal Register[4]. The other components of the system performance standard were used to evaluate the fused silica capillary column with respect to peak assymmetry, acidity/basicity, seperation number, resolution, inertness, and polarity. In addition, the mass spectrometer was tuned each day with perfluorotributylamine (FC-43) according to the manufacterer's recommended procedure.

All volatile and nonvolatile organics were confirmed by comparison of the mass spectra and relative retention time of these constituents in the sample versus those in an external standard. Confirmation of each constituent was indicated when the fit of the mass spectra of the sample with respect to that of the external standard was 850 or higher, and the retention time of the sample peak was within a one minute window of that of the external standard peak as determined by relative retention to an internal standard contained in both the sample and the external standard. The following ten internal standards were contained in the external standard and were spiked into each sample and blank: 1-chloropentane, 1-chlorohexane, 1-chloroheptane, 1-chlorooctane, 1-chlorodecane, 1-chlorododecane, 1-chlorotetradecane, 1-chlorohexadecane, 1-chlorooctadecane, and endosulfan I.

For volatile organic confirmation via the closed loop purging process, 1 liter of water was purged for 30 minutes and the carbon trap extracted with carbon disulfide such that the final extract volume was 10 ul. The GC/MS detection limits and recoveries for this procedure are indicated In Table 5. For the confirmation of solvent extractable hydrocarbons and chlorinated hydrocarbon insecticides, 6 liter samples were extracted with pentane and the extract was concentrated to 300 ul and split into two 150 ul aliquots as described in the solvent extraction procedure. One 150 ul aliquot of the extract was further concentrated to 15 ul at which point GC/MS analysis for solvent extractable hydrocarbons was performed using standard electron impact detection. This same extract was further concentrated from 15 ul to 4 ul for GC/MS analysis of solvent extractable chlorinated hydrocarbon insecticides using multiple ion detection (MID). The GC/MS detection limits and recoveries for the solvent extractable hydrocarbons and chlorinated hydrocarbon insecticides are present in Tables 6 and 7.

TABLE 5. GC/MS STANDARD CONCENTRATIONS, RECOVERIES, AND DETECTION LIMITS FOR QUALITATIVE VOLATILE ORGANIC CONFIRMATION VIA CLOSED LOOP PURGING

COMPOUND	STANDARD CONC (mg/l)	GROB RECOVERY (%)	METHOD * DETECTION LIMIT (ng/l)
Chloroform	1.5	4.7	18
Bromodichloromethane	2.0	9.1	15
Dibromochloromethane	3.7	20.3	12
Bromoform	7.2	28.3	33
1,2-Dichloroethane	1.9	1.2	103
Trichloroethylene	2.2	36.5	2

* Measured at 2x noise level with percent recoveries applied.

TABLE 6. GC/MS STANDARD CONCENTRATIONS, RECOVERIES, AND DETECTION LIMITS FOR SOLVENT EXTRACTABLE HYDROCARBON CONFIRMATION.

COMPOUND	STANDARD CONC (mg/l)	GC/MS * RECOVERY (%)	GC/MS METHOD** DETECTION LIMIT (ng/l)
ethylbenzene	1.0	34.0	2.9
m & p-xylene	1.0	36.0	1.9
o-xylene	1.0	40.2	1.7
cumene	1.0	39.4	2.5
3-ethyltoluene	1.0	42.2	1.2
4-ethyltoluene	1.0	39.0	1.3
1,3,5-trimethylbenzene	1.0	46.5	1.1
2-ethyltoluene	1.0	43.4	1.1
1,2,4-trimethylbenzene	1.0	47.1	1.1
decane	1.0	18.9	3.5
1,3-dichlorobenzene	1.5	46.5	1.1
octanal	1.5	53.2	2.7
1,4-dichlorobenzene	1.5	47.3	0.9
1,2,3-trimethylbenzene	1.5	47.3	2.1
p-cymene	1.0	43.5	1.1
1,2-dichlorobenzene	1.5	48.5	1.0
indene	1.0	45.8	1.4
1,3-diethylbenzene	1.2	44.8	0.4
1,4-diethylbenzene	0.8	43.5	0.6

*Reduced recovery resulting from extract volume reduction to 15 ul.

**Measured at 2x noise level with percent recoveries applied.

TABLE 6. (Cont.)

COMPOUND	STANDARD CONC (mg/l)	GC/MS * RECOVERY (%)	GC/MS METHOD** DETECTION LIMIT (ng/l)
nitrobenzene	1.0	21.2	5.3
d-fenchone	1.4	49.1	0.9
undecane	1.0	19.5	1.7
nonanal	1.5	48.4	1.0
1,2,4,5-tetramethyl -benzene	1.0	47.9	0.7
1,2,3,5-tetramethyl -benzene	0.9	47.9	0.9
1,2,3,4-tetramethyl -benzene	1.0	49.0	0.7
tetralin	1.0	50.6	0.6
2-nitrotoluene	1.6	44.5	2.5
1,2,4-trichlorobenzene	1.5	52.8	0.9
naphthalene	1.0	51.2	0.7
dodecane	1.0	20.5	1.6
1-chloro-4-nitrobenzene	3.0	43.9	0.6
1-chloro-2-nitrobenzene	3.0	40.3	0.8
2-methylnaphthalene	1.0	51.8	0.2
1-methylnaphthalene	1.0	51.7	0.3
cyclohexylbenzene	1.0	50.8	0.7
biphenyl	1.0	53.3	0.6
2-ethylnaphthalene	1.0	52.0	0.3
2,6-dimethylnaphthalene	1.0	53.3	0.6
2,3-dimethylnaphthalene	1.0	54.8	0.6
1,2-dimethylnaphthalene	1.0	10.2	4.8
acenaphthene	1.0	52.5	0.5
pentadecane	1.0	34.8	0.9
2,4-dinitrotoluene	3.0	24.8	13.3
fluorene	1.0	62.9	0.5
hexadecane	1.0	43.7	0.7
diethylphthalate	3.0	48.3	2.1
tributylphosphate	2.0	7.8	25.7
heptadecane	1.0	57.0	0.6
4-nonylphenol	1.0	41.3	2.4
atrazine	4.0	8.9	15.1
dipropylphthalate	2.7	56.6	3.2
phenanthrene	1.0	78.3	0.4
anthracene	1.6	71.4	1.0
diisobutylphthalate	2.1	44.0	4.7

---

*Reduced recovery resulting from extract volume reduction to 15 ul.

**Measured at 2x noise level with percent recoveries applied.

TABLE 6. (Cont.)

COMPOUND	STANDARD CONC (mg/l)	GC/MS * RECOVERY (%)	METHOD** DETECTION LIMIT (ng/l)
nonadecane	1.1	71.3	0.5
alachlor	2.5	32.8	6.5
dibutylphthalate	2.0	73.0	0.5
eicosane	1.1	71.5	0.5
triphenylmethane	1.7	86.0	0.3
fluoranthene	2.0	81.6	0.8
pyrene	2.0	76.4	0.9
1,2-butylbenzylphthalate	2.6	35.7	4.7
bis-[2-ethylhexyl]-phthalate	2.0	49.2	2.0
dioctylphthalate	2.0	48.2	2.8

---

*Reduced recovery resulting from extract volume reduction to 15 ul.

**Measured at 2x noise level with percent recoveries applied.

TABLE 7. GC/MS STANDARD CONCENTRATIONS, RECOVERIES, AND DETECTION LIMITS FOR CHLORINATED HYDROCARBON INSECTICIDE CONFIRMATION.

COMPOUND	STANDARD CONC (mg/l)	GC/MS RECOVERY (%)	GC/MS METHOD** DETECTION LIMIT (ng/l)
α-BHC	5.0	62.8	0.14
hexachlorobenzene	5.0	60.8	0.11
β-BHC	20.0	78.4	0.85
γ-BHC	5.0	75.8	0.23
pentachloronitrobenzene	5.0	72.3	0.92
heptachlor	5.0	72.6	0.31
α-chlordene	11.0	73.7	0.33
aldrin	10.0	68.8	0.33
γ-chlordene	20.0	76.7	0.30
β-chlordene	20.0	76.6	0.26
DCPA	20.0	91.8	0.48
heptachlorepoxide	16.0	86.3	0.82
oxy-chlordane	20.0	85.2	0.44

---

*Reduced recovery resulting from extract volume reduction to 4 ul.

**Measured at 2x noise level with percent recoveries applied.

TABLE 7. (Cont.)

COMPOUND	STANDARD CONC (mg/l)	GC/MS RECOVERY (%)	GC/MS METHOD** DETECTION LIMIT (ng/l)
γ-chlordane	15.0	82.9	0.97
o,p'-DDE	20.0	84.8	2.04
α-chlordane	32.0	90.4	3.98
dieldrin	24.0	87.3	0.61
p,p'-DDE	20.0	88.5	0.42
o,p'-DDD	40.0	86.6	0.51
endrin	40.0	87.5	5.03
endosulfan II	16.0	90.2	2.37
m,p'-DDD	23.8	90.7	0.29
perthane	43.0	92.4	0.48
p,p'-DDD	38.0	81.8	0.23
o,p'-DDT	45.0	91.0	0.35
p,p'-DDT	50.0	96.4	0.15

---

*Reduced recovery resulting from extract volume reduction to 4 ul.

**Measured at 2x noise level with percent recoveries applied.

Heterotrophic Plate Count, Total Coliform, and Dissolved Oxygen --

Analyses for heterotrophic plate count, total coliform, and dissolved oxygen were performed according to Standard Methods[5]. The membrane electrode method was used to measure dissolved oxygen.

Bacterial Speciation --

Speciation was performed on Gram stain isolates originating from the heterotrophic plate count using API 20E enterobacteriaceae strips available from Analytab Products, Plainview, N.Y. for the identification of enterobacteriaceae and other gram negative bacteria. The Gram stain procedure was performed according to Standard Methods[5].

Disinfectant Residuals --

All disinfectant residuals were measured via the LaMotte-Palin DPD-FAS Method using a LaMotte Model DT Laboratory titration outfit available from LaMotte Chemical Products, Chestertown, MD. The stock standard solution of ferrous ammonium sulfate (FAS) was freshly prepared each month and standardized against a primary standard dichromate solution as indicated in the 15th Edition of Standard Methods[5].

Quality Assurance

In order to maintain instrument reliability, maintenance contracts were obtained on all instruments and computers except for the gas chromatographs which were repaired in-house with stocked spare parts. In addition back-up gas chromatographs were made available when required. Instrument operation was checked each eight hour shift by the injection of a calibration standard for all organic analyses except for that of the solvent extractable organics which was injected once each day. These calibration standards were prepared daily for the volatile organics analysis from aliquots of stock standard which were replaced at least once per week. Volatile stock standards were prepared on a quarterly basis and placed in 25 stock standard vials and stored at 4°C prior to use. All other calibration standards for organic analyses were prepared annually with aliquots of each standard stored at 4°C prior to use. Analytical blanks were analyzed once each day for all organic analyses except for the solvent extractable organics which were performed on a weekly basis.

The quality of the data obtained from the analytical measurements performed was assessed in terms of precision, accuracy, completeness, representativeness, and comparibility. Precision was measured by analyzing and comparing the results of duplicate analyses. One duplicate sample was analyzed for each set of samples analyzed (approximately one each week). The sample which was analyzed in duplicate was the first and the last sample to be analyzed within each sample set. In this manner, the precision determined was indicative of the entire sample set over the time period in which the sample set was analyzed. All gas chromatography samples were spiked with one or more internal standards to insure greater precision. The average precision observed for each organic parameter monitored during the operational period is presented in Table 8 along with the concentration range and the number of duplicate sample observations. The number of observations for each parameter varied with sampling frequency and detectability. The percent relative deviation (PRD) of each duplicate was calculated by determining the percent difference between the higher of the two data points (H) and their mean (X), PRD = 100(H-X)/X. The average percent relative deviation represents the average of all of the relative deviations determined for each duplicate across the one year operational period. For example, the average percent relative deviation of 3.8% observed for TOC in Table 8 indicates that all of the TOC data was, on the average, only 3.8% from the mean. The variability of the TOX data was slightly higher with an average percent relative deviation of 5.2% while those for the volatile organics were on the average less than 15%. Bromoform is not listed in Table 8 because it was not detected in any of the duplicate samples analyzed. The percent relative deviations observed for the solvent extractable hydrocarbons and the chlorinated hydrocarbon insecticides were for the most part less than 20%. However, the percent relative deviations of 28% of these substances exceeded a value of 20% while 15% exceeded a value of 25%. Those compounds whose average percent relative deviation exceeded 30% were 1,3-dichlorobenzene, octanal, dipropylphthalate, anthracene, bis-[2-ethylhexyl]-phthalate, dioctylphthalate, m,p'-DDD, and o,p'-DDT. A close examination of the semivolatile solvent extractable organic data indicated that a definite correlation existed between the area of the chromatographic peak and the percent relative deviation observed for the duplicate sample. For example, the percent relative error determined for the internal standards of the hydrocarbon analyses which had considerably higher concentrations and thus higher areas than those of the compounds of interest, were all consistently below 5% while those for the compounds of interest were all consistently above 15% with an occassional excursion above 100%. A composite comparison of chromatographic peak area with percent relative deviation for all of the duplicate analyses performed during the operational period for the solvent extractable chlorinated hydrocarbon insecticides and hydrocarbons are presented in Figures 6 and 7, respectively. Despite the presence of a few outlying data points, these comparisons indicate that a threshold area existed for this type of analysis below which the precision observed was considerably erratic. This comparison also shows that as the area of the chromatographic peak increased, the percent relative deviation also decreased. Based upon this variability, the majority of the semivolatile solvent extractable hydrocarbon and chlorinated hydrocarbon insecticide results can only be considered to be of a semi-quantitative nature.

Accurracy was assessed through the evaluation of the relative error determined for the internal quality control samples obtained from EPA and through performance audits conducted by EPA. Internal quality control samples were introduced into the sample analysis scheme once each month while EPA performance audits were conducted every six months. While each internal quality control or EPA performance audit sample did not contain all of the compounds being monitored by a particular analytical procedure, those compounds contained in the quality assurance sample were considered representative of those substances being

---

TABLE 8. ANALYTICAL PRECISION AS MEASURED BY DUPLICATE SAMPLE ANALYSIS.

PARAMETER	CONC. RANGE	NO. OF OBSERV.	AVERAGE PERCENT RELATIVE DEVIATION
TOC (mg/l)	2.16-4.23	53	3.8
TOX (ug/l)	67-168	27	5.2
chloroform (ug/l)	2.0-4.5	51	4.9
bromodichloromethane (ug/l)	0.34-10.7	49	5.0
dibromochloromethane (ug/l)	0.06-0.50	36	10.7
1,2-dichloroethane (ug/l)	0.04-6.9	43	13.7
ethylbenzene (ng/l)	0.82-1780	29	27.7
p-xylene+m-xylene (ng/l)	6-246	39	27.6
o-xylene (ng/l)	4-2419	43	17.7
cumene (ng/l)	0.2-807	29	14.3
3-ethyltoluene (ng/l)	2-50	35	17.4
4-ethyltoluene (ng/l)	0.1-148	37	20.6
1,3,5-trimethylbenzene (ng/l)	3-34	42	18.4
2-ethyltoluene (ng/l)	0.2-16	43	20.2
1,2,4-trimethylbenzene (ng/l)	8-81	43	17.1
decane (ng/l)	0.9-16	38	25.0
1,3-dichlorobenzene (ng/l)	0.9-11	30	33.9
octanal (ng/l)	1-11	34	36.1
1,4-dichlorobenzene (ng/l)	2-53	43	13.6
1,2,3-trimethylbenzene (ng/l)	2-24	43	16.3
p-cymene (ng/l)	0.4-24	40	22.0
1,2-dichlorobenzene (ng/l)	1-65	41	12.7
indene (ng/l)	1-12	43	16.6
1,3-diethylbenzene (ng/l)	0.3-22	41	20.8
1,4-diethylbenzene (ng/l)	0.2-11	38	19.4
nitrobenzene (ng/l)	1-48	35	14.3
d-fenchone (ng/l)	0.3-24	40	11.1
undecane (ng/l)	0.1-8.8	39	28.4
nonanal (ng/l)	1-36	43	15.7
1,2,4,5-tetramethylbenzene (ng/l)	0.9-15	43	14.0
1,2,3,5-tetramethylbenzene (ng/l)	1-13	41	14.7
1,2,3,4-tetramethylbenzene (ng/l)	0.7-11	43	15.7
tetralin (ng/l)	0.3-34	43	17.7
2-nitrotoluene (ng/l)	0.07-7	41	15.0
1,2,4-trichlorobenzene (ng/l)	0.1-20	32	18.3
naphthalene (ng/l)	5-55	43	17.0
dodecane (ng/l)	0.6-13	42	21.2
1-chloro-4-nitrobenzene (ng/l)		43	7.3
1-chloro-2-nitrobenzene (ng/l)	5-283	43	8.3
2-methylnaphthalene (ng/l)	6-73	43	15.5
1-methylnaphthalane (ng/l)	3-46	43	15.4

TABLE 8. (CONT'D)

PARAMETER	CONC. RANGE	NO. OF OBSERV.	AVERAGE PERCENT RELATIVE DEVIATION
cyclohexylbenzene (ng/l)	0.3-21	39	18.5
biphenyl (ng/l)	0.5-15	42	14.4
2-ethylnaphthalene (ng/l)	2-49	43	19.1
2,6-dimethylnaphthalene (ng/l)	2-59	43	18.7
2,3-dimethylnaphthalene (ng/l)	0.9-29	43	15.2
1,2-dimethylnaphthalene (ng/l)	0.2-63	42	14.2
acenaphthene (ng/l)	1-28	43	14.3
pentadecane (ng/l)	1-30	42	14.9
2,4-dinitrotoluene (ng/l)	1-61	41	18.6
fluorene (ng/l)	0.7-23	43	19.6
hexadecane (ng/l)	0.9-12	41	16.1
diethylphthalate (ng/l)	29-71	42	15.7
tributylphosphate (ng/l)	9-211	43	12.0
heptadecane (ng/l)	3-26	43	10.8
4-nonalphenol (ng/l)	6-131	40	13.1
atrazine (ng/l)	13-234	43	14.6
dipropylphthalate (ng/l)	0.3-11	26	30.8
phenanthrene (ng/l)	2-39	42	17.8
anthracene (ng/l)	0.2-20	37	33.2
diisobutylphthalate (ng/l)	2-11	43	18.3
nonadecane (ng/l)	1-5	42	19.1
alachlor (ng/l)	16-559	43	9.2
dibutylphthalate (ng/l)	14-295	43	28.4
eicosane (ng/l)	2-185	38	19.6
triphenylmethane (ng/l)	0.5-10	41	19.7
fluoranthene (ng/l)	1-11	39	25.8
pyrene (ng/l)	0.9-21	42	24.3
1,2-butylbenzylphthalate (ng/l)	1-28	42	23.5
bis[2-ethylhexyl]phthalate (ng/l)	0.8-239	40	32.5
dioctylphthalate (ng/l)	9-97	35	30.8
α-BHC (ng/l)	1.2-9.7	22	6.6
hexachlorobenzene (ng/l)	0.44-1.7	22	5.8
β-BHC (ng/l)	0.72-4.3	22	9.9
γ-BHC (ng/l)	0.54-7.6	22	4.6
pentachloronitrobenzene (ng/l)	0.11-0.93	21	17.9
heptachlor (ng/l)	0.04-34	21	11.1
α-chlordene (ng/l)	0.05-0.78	22	17.8
aldrin (ng/l)	0.10-1.5	22	11.8
γ-chlordene (ng/l)	0.02-1.3	22	11.1
β-chlordene (ng/l)	0.05-32	21	13.9
DCPA (ng/l)	0.19-6.1	22	9.5
heptachlor epoxide (ng/l)	0.25-2.1	22	8.7
oxy-chlordane (ng/l)	0.01-0.26	21	23.6
γ-chlordane (ng/l)	0.21-0.49	22	8.5

TABLE 8. (CONT'D)

PARAMETER	CONC. RANGE	NO. OF OBSERV.	AVERAGE PERCENT RELATIVE DEVIATION
o,p'-DDE (ng/l)	0.09-0.76	21	17.0
a-chlordane (ng/l)	0.12-0.33	22	10.6
dieldrin (ng/l)	1.2-5.3	22	5.6
p,p'-DDE (ng/l)	0.07-0.33	22	14.2
o,p'-DDD (ng/l)	0.14-1.3	22	18.5
endrin (ng/l)	0.32-1.8	22	12.7
endosulfan II (ng/l)	0.01-2.2	22	25.7
m,p'-DDD (ng/l)	0.06-9.53	13	49.8
perthane (ng/l)	0.74-20	19	20.7
p,p'-DDD (ng/l)	0.18-1.1	21	20.8
o,p'-DDT (ng/l)	0.02-0.36	15	38.8
p,p'-DDT (ng/l)	0.03-1.0	20	28.8

monitored. The average percent relative error observed for each organic compound contained in the internal quality control samples analyzed during the one year operational period is presented in Table 9. Quality control samples for TOX were unavialable from EPA, therefore, none were analyzed. As indicated, all of the average relative errors of the internal control samples were within the standard 20% acceptable range used by EPA except for p,p'-DDE and p,p'-DDT. The relative error observed for these substances outside of the 20% window was attributable to the partial decomposition of p,p'-DDT to p,p'-DDE in the injection port or on the capillary column of the gas chromatograph. The results of the EPA performance audits conducted before, during, and at the end of the pilot column operational period are presented in Tables 10, 11, and 12, respectively. The acceptance limits indicated are based on 20% of the true value. The higher concentration performance sample results for bromodichloromethane and dibromochloromethane which were analyzed prior to the operational period, were marginally unacceptable as were those of the low concentration performance samples for dibromochloromethane and bromoform which were analyzed at the end of the operational period. All other performance evaluation results were within the acceptable range.

GC/MS Qualitative Confirmation

Qualitative confirmation by GC/MS was performed on volatile organics and solvent extractable hydrocarbons observed in the influent of each pilot column process stream after 30 minutes of

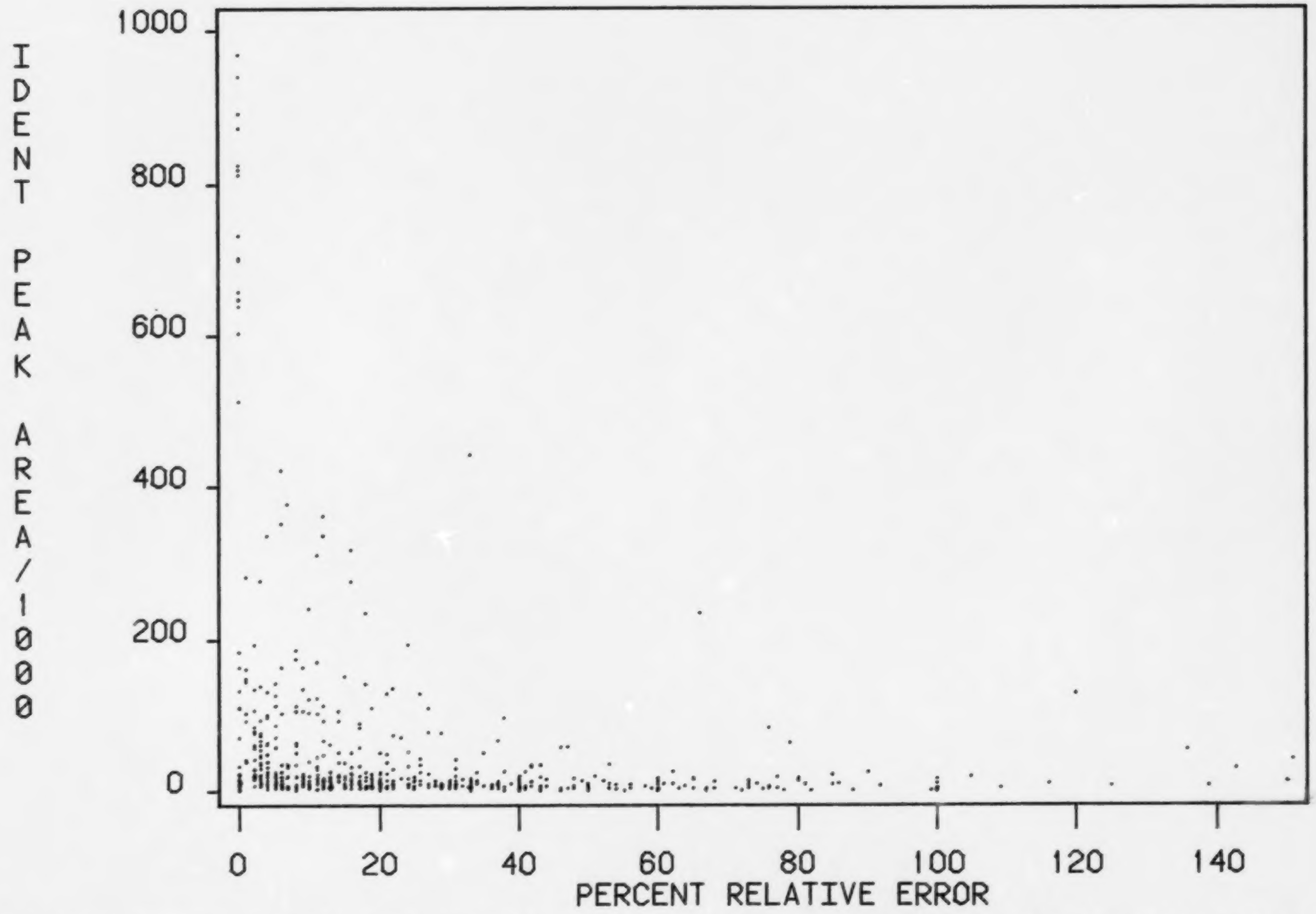


Figure 6. Comparison of Identified Peak Area Versus Percent Relative Deviation of the Duplicate Solvent Extractable Chlorinated Hydrocarbon Insecticide Analyses.

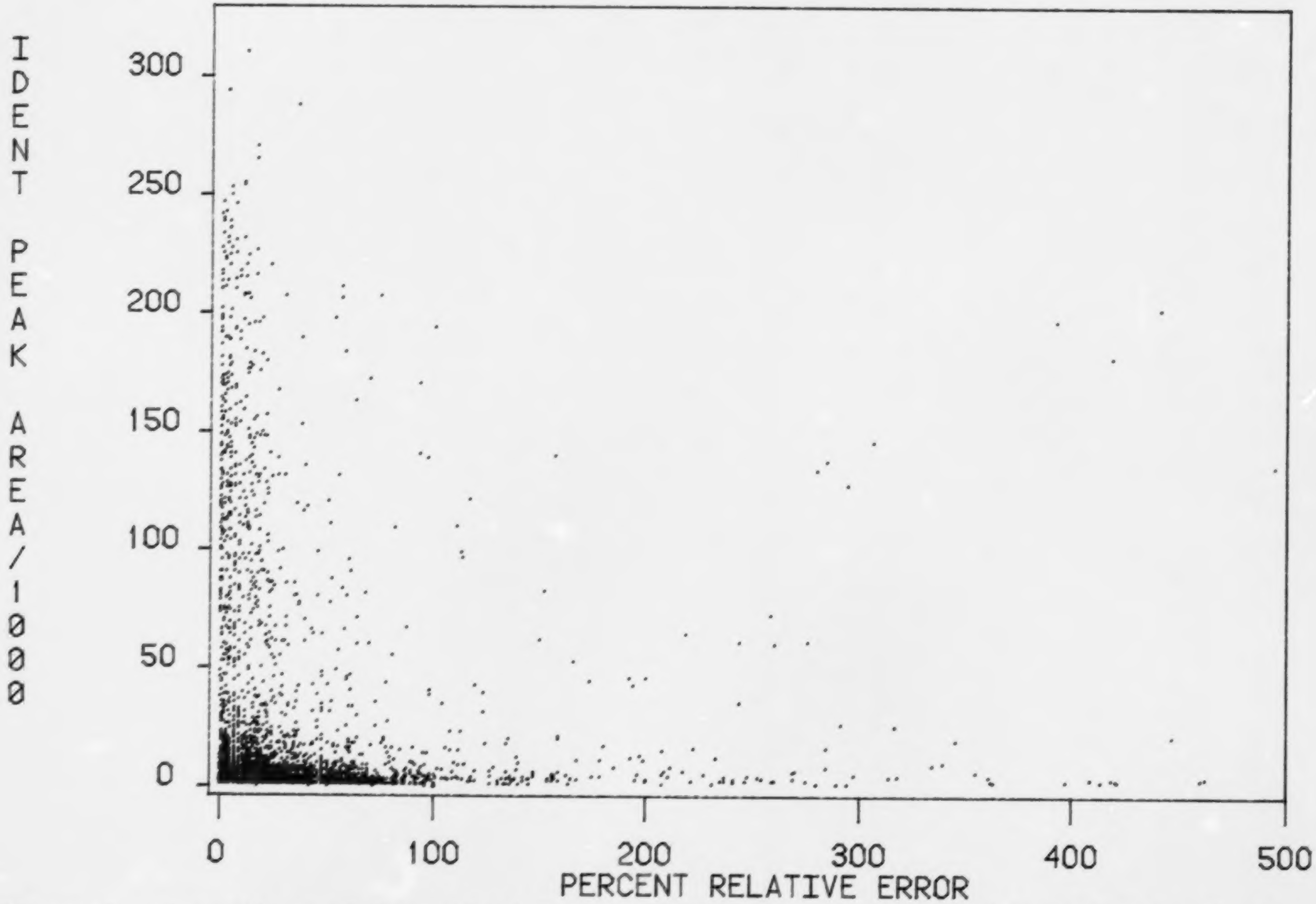


Figure 7. Comparison of Identified Peak Area Versus Percent Relative Deviation of the Duplicate Solvent Extractable Hydrocarbon Analyses.

TABLE 9. ANALYTICAL ACCURACY AS MEASURED BY INTERNAL QUALITY CONTROL SAMPLE ANALYSIS.

PARAMETER	CONCENTRATION RANGE (ug/l)	NO. OF OBSERV.	AVERAGE % RELATIVE ERROR
TOC	4.1 & 61.2	7	3.9
chloroform	11.0-59.6	14	4.1
bromodichloromethane	1.7-40.0	11	11.4
dibromochloromethane	2.4-16.9	13	9.6
bromoform	1.3-10.4	13	7.6
1,2-dichloroethane	1.5 & 20.0	3	5.8
1,2-dichlorobenzene	7.2	2	0.0
1,3-dichlorobenzene	2.7	2	5.5
1,4-dichlorobenzene	3.3	2	7.5
1,2,4-trichlorobenzene	11.0	2	1.0
dimethylphthalate	30 & 85	2	6.0
diethylphthalate	60 & 115	2	4.5
dibutylphthalate	70 & 160	2	4.5
butylbenzylphthalate	25 & 85	2	12.0
bis-[2-ethylhexyl]-phthalate	85 & 130	2	1.0
dioctylphthalate	20 & 210	2	10.0
naphthalene	30 & 75	2	2.5
acenaphthene	55 & 71	3	6.7
phenanthrene	38 & 55	2	5.0
anthracene	56 & 113	2	8.0
fluoranthene	19 & 94	2	2.5
pyrene	19 & 139	2	18.0
γ-BHC	0.09 & 0.40	10	20.0
aldrin	0.056	2	19.5
heptachlor	0.028	2	10.5
dieldrin	0.114	2	6.5
endrin	0.22 & 1.69	10	19.1
p,p'-DDE	0.013	2	215
p,p'-DDD	0.170	2	4.5
p,p'-DDT	0.156	2	25.0

TABLE 10. USEPA PERFORMANCE EVALUATION STANDARDS WSO12 MAY 1983.

PARAMETER	VIAL NO.	TRUE VALUE (ug/l)	REPORTED VALUE (ug/l)	ACCEPTANCE LIMITS (ug/l)	PERFORMANCE EVALUATION
chloroform	1	5.93	5.93	4.74-7.12	acceptable
	2	35.6	37.24	28.5-42.7	acceptable
bromodichloro-methane	1	14.1	15.05	11.3-16.9	acceptable
	2	42.3	51.19	33.8-50.8	unacceptable
dibromochloro-methane	1	27.9	31.38	22.3-33.5	acceptable
	2	55.8	57.98	44.6-67.0	unacceptable
bromoform	1	30.5	28.67	24.4-36.6	acceptable
	2	67.7	70.62	54.2-81.2	acceptable
total trihalomethane	1	78.[illegible]3	81.03	62.7-94.1	acceptable
	2	201.4	227.03	161-242	acceptable

TABLE 11. USEPA PERFORMANCE EVALUATION STANDARDS WS013 OCTOBER 1983.

PARAMETER	VIAL NO.	TRUE VALUE (ug/l)	REPORTED VALUE (ug/l)	ACCEPTANCE LIMITS (ug/l)	PERFORMANCE EVALUATION
chloroform	1	71.2	75.54	57.0-85.4	acceptable
	2	23.7	23.46	19.0-28.4	acceptable
bromodichloro-methane	1	56.4	65.87	45.1-67.7	acceptable
	2	13.3	20.35	15.0-22.6	acceptable
dibromochloro-methane	1	39.0	42.65	31.2-46.8	acceptable
	2	11.2	12.87	8.96-13.4	acceptable
bromoform	1	50.8	55.96	40.6-61.0	acceptable
	2	27.1	26.95	21.7-32.5	acceptable
total trihalomethane	1	217.4	240.0	174-261	acceptable
	2	80.8	83.63	64.6-97.0	acceptable
endrin	1	0.130	0.179	0.132-0.222	acceptable
	2	4.54	5.69	2.18-6.13	acceptable
γ-BHC	1	0.690	0.937	0.354-0.941	acceptable
	2	2.63	3.25	1.59-3.29	acceptable

TABLE 12. USEPA PERFORMANCE EVALUATION STANDARDS WS014 MAY 1984.

PARAMETER	VIAL NO.	TRUE VALUE (ug/l)	REPORTED VALUE (ug/l)	ACCEPTANCE LIMITS (ug/l)	PERFORMANCE EVALUATION
chloroform	1	11.9	10.64	9.52-14.3	acceptable
	2	47.5	48.64	38.0-57.0	acceptable
bromodichloromethane	1	9.40	8.09	7.52-11.3	acceptable
	2	70.5	80.58	56.4-84.6	acceptable
dibromochloromethane	1	16.7	12.73	13.4-20.0	unacceptable
	2	61.3	59.21	49.0-73.6	acceptable
bromoform	1	20.3	14.83	16.2-24.4	unacceptable
	2	50.8	47.63	40.6-61.0	acceptable
total trihalomethane	1	58.3	46.29	46.6-70.0	unacceptable
	2	23.01	236.1	184-276	acceptable
endrin	1	1.82	1.95	1.15-2.33	acceptable
	2	0.731	0.617	0.458-0.911	acceptable
γ-BHC	1	5.58	6.19	3.06-7.21	acceptable
	2	0.439	0.458	0.250-0.621	acceptable

disinfectant contact time. Through an over sight, confirmation of volatile organics was not begun until the tenth week of pilot column operation. Chlorinated hydrocarbon insecticide confirmation by GC/MS was performed only on the nondisinfected influent to the pilot column system. Approximately 44 volatile organic samples, 52 solvent extractable hydrocarbon samples and 27 chlorinated hydrocarbon insecticide samples were confirmed by GC/MS for each sampling location. The percentage of possible GC/MS confirmation along with the average mass spectral fit of each volatile organic and solvent extractable hydrocarbon are presented in Table 13 while those for the solvent extractable chlorinated hydrocarbon insecticides are presented in Table 14. A value of 1000 for mass spectral fit would mean that the mass spectra of the sample perfectly matched that in the computer based mass spectral library.

In general, the level of confirmation was dependent upon several factors: 1) the comparative levels of detection of the GC and GC/MS methologies used, 2) coeluting substances resulting in apparent higher GC concentrations which exceed the GC/MS detection limit, and, 3) the amount of GC/MS spectral interference present in relation to the GC/MS detection limit. Any one of these factors or a combination thereof could result in a particular substance being quantitated by GC but unconfirmed by GC/MS.

The level of confirmation observed for the volatile organic substances was resonably good with all confirmations greater than 80%. The confirmation of solvent extractable hydrocarbons ranged from 0-100% with the majority of confirmations being greater than 80%. Those substances which were essentialy unconfirmed were tetralin, cyclohexylbenzene, dipropylphthalate, and triphenylmethane. The majority of the unconfirmed GC analysis results of the solvent extractable hydrocarbons were less than or equal to their respective GC/MS detection limits. However, several of the GC results of these compounds were greater than their respective GC/MS detection limits suggesting the intermittant coelution of interfering substances. The percentage of confirmation for the majority of the solvent extractable hydrocarbons monitored in the ozone influent were considerable lower than those of the other process streams due to the partial removals of these substances by ozonation which resulted in concentrations below the GC/MS detection limits.

TABLE 13. PERCENT OF POSSIBLE GC/MS CONFIRMATION AND AVERAGE MASS SPECTRAL FIT OF VOLATILE ORGANICS AND SOLVENT EXTRACTABLE HYDROCARBONS IN THE INFLUENT OF EACH PROCESS STREAM.

COMPOUND	NONDISIN %/FIT	OZONE %/FIT	ClO2 %/FIT	NH_2Cl %/FIT	CHLORINE %/FIT
chloroform	95/892	83/917	86/901	98/926	100/925
bromodichloromethane	83/969	94/973	100/978	93/985	100/977
dibromochloromethane	100/992	NF[1]	100/972	100/982	100/977
1,2-dichloroethane	97/814	89/832	100/830	97/818	94/835
trichloroethylene	NF	NF	NF	100/994	100/994
ethylbenzene	92/983	75/968	90/975	92/987	93/966
m & p-xylene	96/985	93/950	92/976	98/975	94/981
o-xylene	96/965	77/958	88/967	96/963	87/955
cumene	87/879	35/923	80/919	85/920	77/904
3-ethyltoluene	93/977	80/969	89/973	96/970	88/957
4-ethyltoluene	93/916	72/896	88/934	86/924	88/907
1,3,5-trimethylbenzene	90/922	76/890	87/921	96/922	86/901
2-ethyltoluene	88/884	71/869	87/893	90/890	87/899
1,2,4-trimethylbenzene	94/970	79/964	92/960	94/963	88/953
decane	80/829	73/790	88/790	92/882	87/848
1,3-dichlorobenzene	59/871	92/911	85/798	85/823	76/851
octanal	76/912	53/967	92/930	79/933	79/977
1,4-dichlorobenzene	88/910	56/879	84/909	86/919	88/911
1,2,3-trimethylbenzene	90/911	59/883	88/906	92/908	86/902
p-cymene	64/753	42/738	59/798	62/774	70/788
1,2-dichlorobenzene	67/939	34/958	67/965	70/974	80/931
indene	86/891	43/879	74/910	81/893	52/896
1,3-diethylbenzene	60/871	33/862	51/924	61/879	59/895
1,4-diethylbenzene	48/777	29/697	53/830	51/803	49/784
nitrobenzene	53/911	21/942	54/932	53/905	56/924
d-fenchone	88/928	65/938	87/930	91/944	80/929
undecane	80/820	59/748	84/777	83/789	88/806
nonanal	96/912	92/965	90/934	85/949	86/924
1,2,4,5-tetra-methylbenzene	90/909	57/879	78/916	86/900	84/892
1,2,3,5-tetra-methylbenzene	94/939	71/882	88/928	90/919	88/905
1,2,3,4-tetra-methylbenzene	88/906	45/838	80/898	82/896	70/895
tetralin	6/804	NC[2]	10/892	10/810	13/851
2-nitrotoluene	71/767	14/657	64/809	64/783	55/836

---

[1] Not found by GC analysis.

[2] Not confirmed by GC/MS analysis.

TABLE 13. (CONT'D)

COMPOUND	NONDISIN %/FIT	OZONE %/FIT	ClO_2 %/FIT	NH_2Cl %/FIT	CHLORINE %/FIT
1,2,4-trichlorobenzene	65/889	28/838	73/880	66/862	55/884
naphthalene	94/967	78/938	96/966	98/963	94/960
dodecane	80/810	66/782	82/766	80/784	72/785
1-chloro-4-nitrobenzene	93/943	63/945	98/942	94/949	92/944
1-chloro-2-nitrobenzene	91/910	53/841	95/906	94/917	84/921
2-methylnaphthalene	98/960	76/923	94/944	98/940	92/938
1-methylnaphthalene	94/949	82/834	92/949	98/939	94/916
cyclohexylbenzene	6/779	NC	6/894	6/638	6/824
biphenyl	87/902	28/862	85/910	87/901	85/896
2-ethylnaphthalene	91/913	20/801	86/932	96/921	83/935
2,6-dimethylnaphthalene	93/944	32/793	87/945	94/936	84/914
2,3-dimethylnaphthalene	85/954	21/861	83/958	91/952	76/939
1,2-dimethylnaphthalene	76/854	50/856	73/846	72/854	73/833
acenaphthene	92/877	7/801	87/876	86/881	49/837
pentadecane	98/918	90/893	95/920	100/913	98/916
2,4-dinitrotoluene	37/850	11/831	38/887	48/845	47/837
fluorene	91/915	22/843	93/918	93/916	93/917
hexadecane	94/944	92/908	96/931	98/931	98/922
diethylphthalate	98/990	100/960	98/990	98/989	100/983
tributylphosphate	98/926	56/901	92/927	96/936	98/928
heptadecane	100/961	98/964	98/975	100/967	98/979
4-nonylphenol	62/915	16/893	58/887	61/885	31/886
atrazine	100/926	60/862	100/934	100/935	98/943
dipropylphthalate	11/826	7/801	22/829	37/814	39/833
phenanthrene	98/953	58/793	96/965	98/948	98/953
anthracene	71/869	2/856	36/836	50/870	35/813
diisobutylphthalate	100/938	98/918	98/936	100/940	100/935
nonadecane	100/933	94/918	98/927	100/927	96/933
alachlor	98/916	71/745	96/915	98/917	98/928
dibutylphthalate	98/988	98/986	100/984	98/989	98/986
eicosane	95/927	90/916	92/927	94/925	92/933
triphenylmethane	NC	2/919	6/701	2/750	NC
fluoranthene	90/888	26/827	93/894	90/885	93/880
pyrene	98/922	20/808	89/914	89/918	88/921
1,2-butylbenzylphthalate	91/910	74/902	90/914	89/918	88/921

---

[1] Not found by GC analysis.

[2] Not confirmed by GC/MS analysis.

TABLE 13. (CONT'D)

COMPOUND	NONDISIN %/FIT	OZONE %/FIT	ClO$_2$ %/FIT	NH$_2$Cl %/FIT	CHLORINE %/FIT
bis-[2-ethylhexyl]-phthalate	98/843	98/822	95/855	100/845	95/854
dioctylphthalate	75/858	74/858	77/869	79/867	77/873

---

[1] Not found by GC analysis.

[2] Not confirmed by GC/MS analysis.

TABLE 14. PERCENT OF POSSIBLE GC/MS CONFIRMATION AND AVERAGE MASS SPECTRAL FIT OF THE CHLORINATED HYDROCARBON INSECTICIDES IN THE INFLUENT OF THE NONDISINFECTED PROCESS STREAM.

COMPOUND	%/FIT	COMPOUND	%/FIT
α-BHC	93/977	γ-chlordane	53/978
hexachlorobenzene	93/963	o,p'-DDE	8/930
β-BHC	15/912	α-chlordane	53/992
γ-BHC	59/956	dieldrin	93/985
pentachloronitrobenzene	4/991	p,p'-DDE	48/985
heptachlor	9/958	o,p'-DDD	57/955
α-chlordene	13/963	endrin	22/978
aldrin	4/869	endosulfan II	12/977
γ-chlordene	46/980	m,p'-DDD	7/996
β-chlordene	8/964	perthane	0/0
DCPA	100/978	p,p'-DDD	54/949
heptachlor epoxide	70/945	o,p'-DDT	38/921
oxy-chlordane	23/952	p,p'-DDT	48/989

SECTION 6

OPERATIONAL PARAMETERS AND CONDITIONS

GRANULAR ACTIVATED CARBON SELECTION

An evaluation of various types of granular activated carbon was undertaken to determine which type was the most efficient in removing the wide spectrum of trace level organic contaminants contained in lower Mississippi River drinking water. Those granular activated carbons evaluated were Calgon's Filtrasorb 400, Carborundum's GAC 40, ICI's Hydrodarco 4000, Norit's Row 0.8 Supra, and Westvaco's WV-G. All of these GACs were 12x40 mesh except for the Norit Row 0.8 Supra which was pelletized with a diameter of 0.8 mm and length which varied from 1-2 mm. With each GAC column's empty bed contact time (EBCT) kept relatively constant and with similiarly observed heterotrophic plate count levels observed in the effluent of each column, the performance of each GAC was evaluated relative to its adsorption efficiency for total organic carbon (TOC), terminal trihalomethanes (THM-FP) instantaneous trihalomethanes (THM-I), 1,2-dichloroethane (DCE), electron capture total area (ECTOAR), and flame ionization total area (FITOAR). ECTOAR and FITOAR represent the total integrated peak areas of the nonvolatile electron capture and flame ionization chromatograms (excluding the solvent front) as compared to that of their respective external standard chromatograms. Complete details of this evaluation are presented in Appendix A.

The results of this six month evaluation indicated that Westvaco's WV-G 12x40 mesh GAC exhibited the highest adsorption efficiency for each trace organics parameter monitored during this study and as such was considered the best GAC for the removal of trace level organic contaminants from lower Mississippi River drinking water. Each of the other GAC types under study exhibited some deficiency in TOC, THM-FP, THM-I and/or DCE adsorption efficiency as indicated in Appendix A.

PHYSICAL OPERATING CONDITIONS

After the clarification of the raw river water with diallyldimethylammoniumchloride and/or dimethylamine polyelectrolyte cationic polymers in the Permuttit III precipitators, clarified water was filtered through one of two pressure sand filters containing 34 inches of 0.45 - 0.60mm filter sand which was operated at an average hydraulic loading of 2.55 gal/min/ft^2 so as to supply the pilot column system with an average influent flow of 12.5 GPM of sand filtered nondisinfected water. The average empty bed contact time of the clarified influent with the sand media of the pressure sand filters was 8.3 minutes.

Following pressure sand filtration, each disinfectant contact chamber received a flow of water which averaged 2.0 GPM for all disinfectant streams and resulted in disinfectant contact times which averaged 31.7 minutes for the ozone stream, 32.1 minutes for the chlorine dioxide stream, 31.4 minutes for the chloramine stream, and 31.8 minutes for the chlorine stream.

After disinfection, each glass pilot column in each process stream received a flow of approximately 0.5 GPM which after passing through a 6.8 ft. bed of sand or GAC media resulted in an empty bed contact time (EBCT) of approximately 20 minutes. To assure the uniformity of the adsorption properties of the GAC in all columns, ten 40 lbs bags of GAC were placed in a stainless steel tank and backwashed to mix the GAC and remove the majority of the GAC fines prior to the GAC being placed in the pilot columns. The average flow rate, hydraulic loading, EBCT, and all backwash information for each pilot column is presented in Table 15. These data indicate that the average flow rates, hydraulic loadings, and EBCTs of all the pilot columns were essentially identical. The backwash frequencies and total backwash volumes used were insignificant as compared to the volume of water filtered. And since the backwash water used was sand filtered nondisinfected water, no significant effect is believed to have occurred with respect to the variations in backwash frequencies and volumes observed.

A further comparison of the actual EBCTs observed for each column of each process stream is presented in Figures 8-12. The data presented represents measurements taken Monday through Friday over the one year operational period of the pilot column system. In general, those data which are off scale indicate a temporary shut down of the pilot column system. These shutdowns were primarily due to power failures or influent pump malfunctions. A greater frequency of shutdowns was observed for the ozone process stream due to malfunctions of the ozone process stream pump. The one week shut down of the entire pilot column system which occurred between day 64 and day 70, resulted from the simultaneous shut down of the two clarification units supplying water to the pilot column system. On or about day 320 the GAC column of the chloramine system was taken out of service as indicated in Figure 11 because the column was severely cracked. The GAC in this column was quantitatively transferred

TABLE 15: PHYSICAL OPERATING CONDITIONS FOR THE PILOT COLUMN SYSTEM DURING THE FIRST YEAR OF OPERATION

LOCATION	AVE FLOW RATE (GPM)	AVERAGE HYDRAULIC LOAD (GAL/ MIN/FT^2)	AVE EBCT (MIN)	TOTAL VOLUME FILTERED (GALX1000)	BACKWASH TOTAL NO.	BACKWASH TOTAL VOL. (GAL)
NONDISINFECTED						
Sand	0.495	2.52	20.2	259	5	100
GAC	0.495	2.52	20.2	259	5	96
GAC Dupl.	0.497	2.53	20.1	261	5	96
OZONE						
Sand	0.487	2.48	20.5	255	3	82
GAC	0.496	2.53	20.2	261	3	61
GAC Dupl.	0.497	2.53	20.1	261	3	56
CHLORINE DIOXIDE						
Sand	0.478	2.43	20.9	248	4	97
GAC	0.489	2.49	20.4	256	3	83
GAC Dupl.	0.494	2.52	20.2	258	3	80
CHLORAMINE						
Sand	0.494	2.52	20.2	257	4	85
GAC	0.494	2.52	20.2	258	5	127
GAC Dupl.	0.496	2.53	20.2	261	4	87
CHLORINE						
Sand	0.496	2.53	20.2	260	4	104
GAC	0.495	2.52	20.2	259	3	75
GAC Dupl.	0.493	2.51	20.3	258	3	79

into a spare column which was placed back into service. No significant variations in etfluent water quality were observed for any parameter after this transfer.

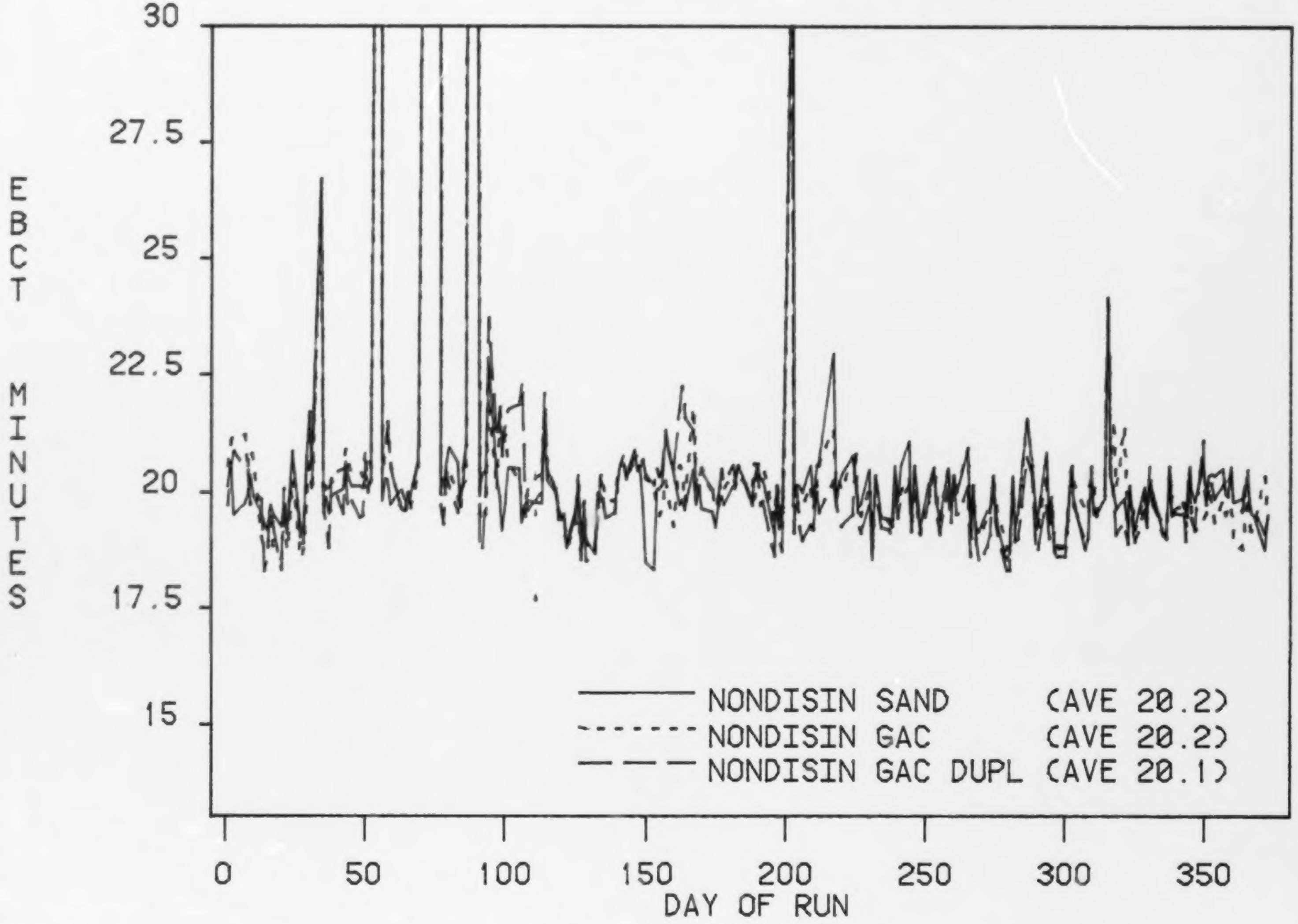


Figure 8. Empty Bed Contact Times Observed for the Nondisinfected Process Stream.

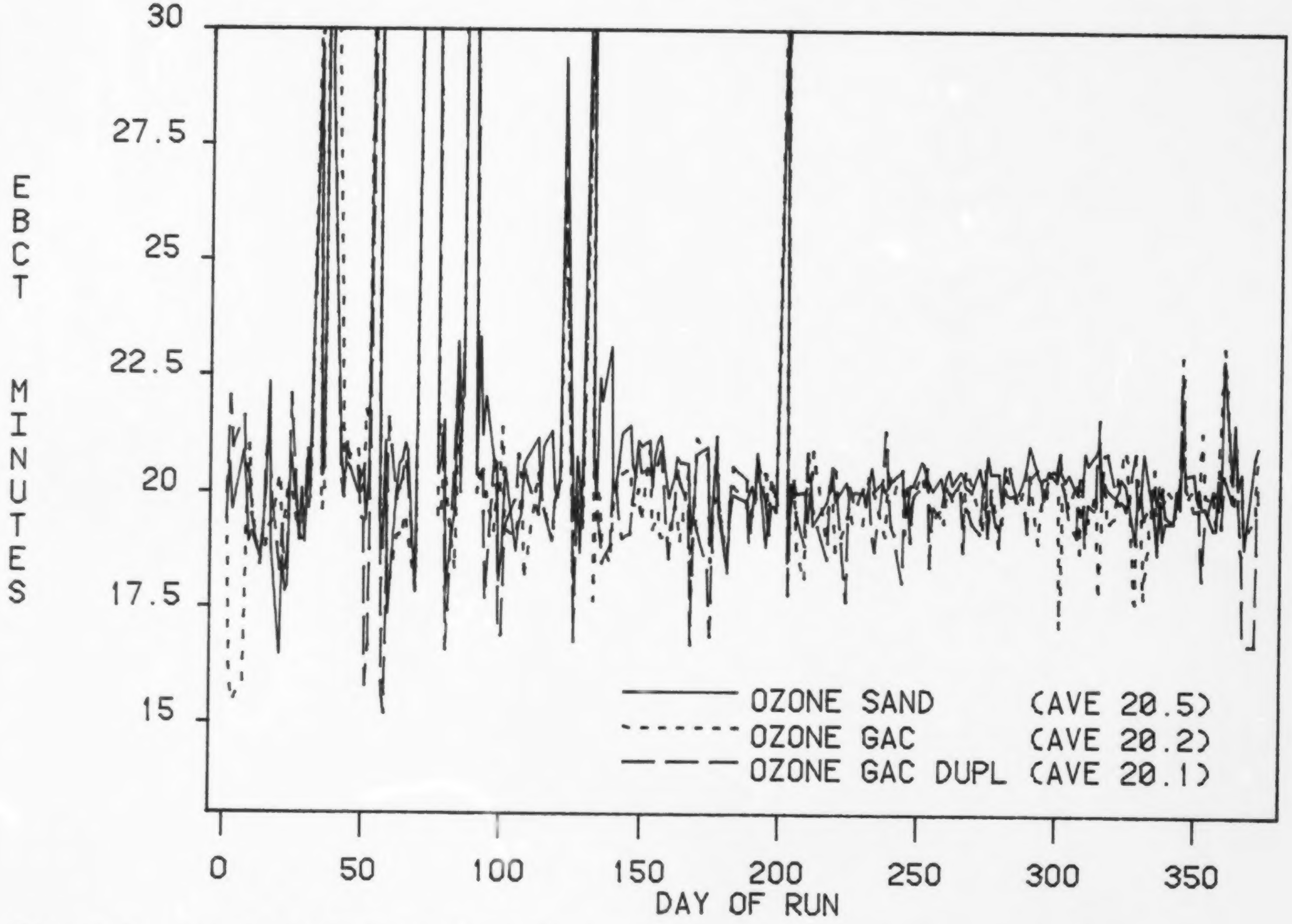


Figure 9. Empty Bed Contact Times Observed for the Ozone Process Stream.

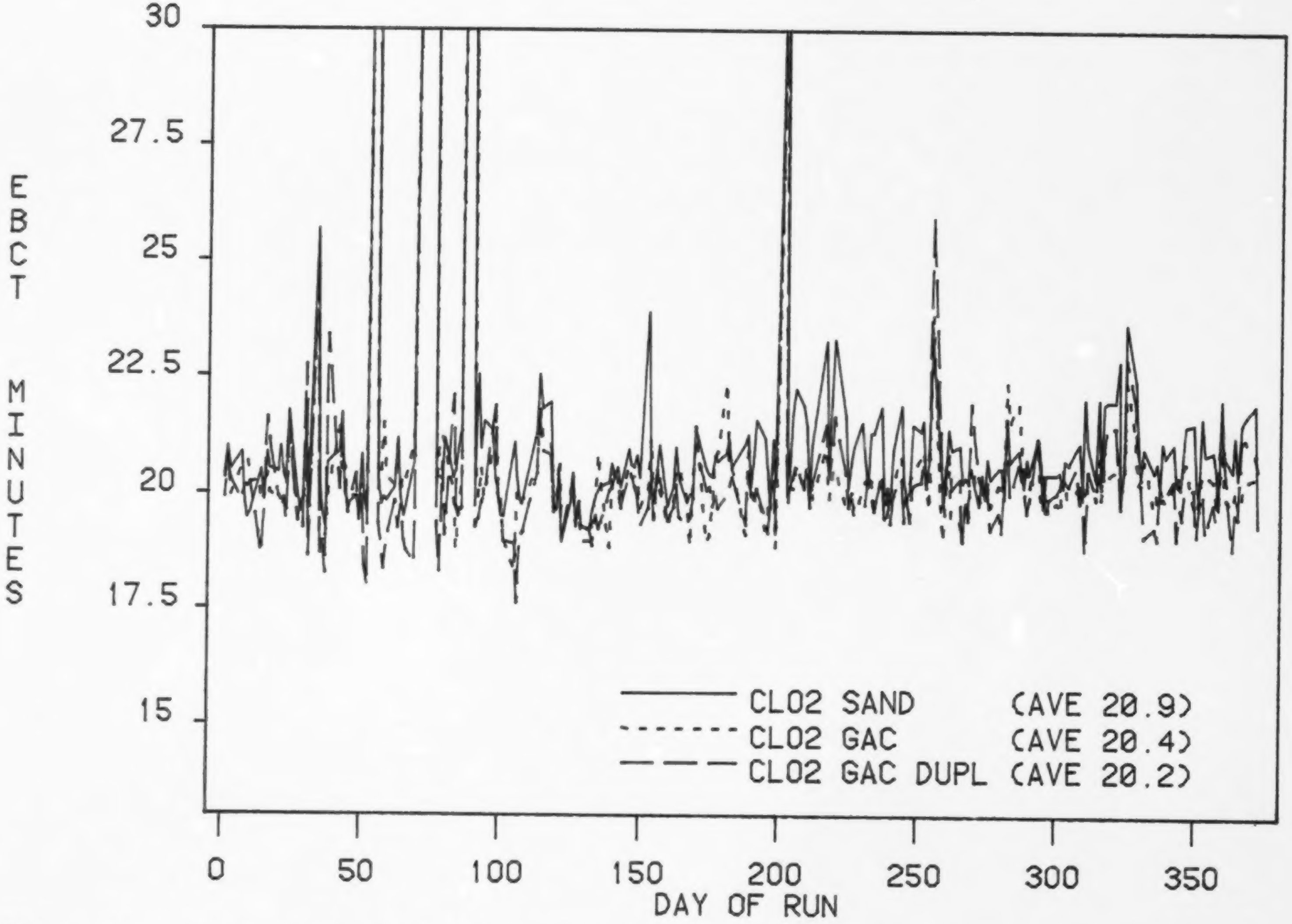


Figure 10. Empty Bed Contact Times Observed for the Chlorine Dioxide Process Stream.

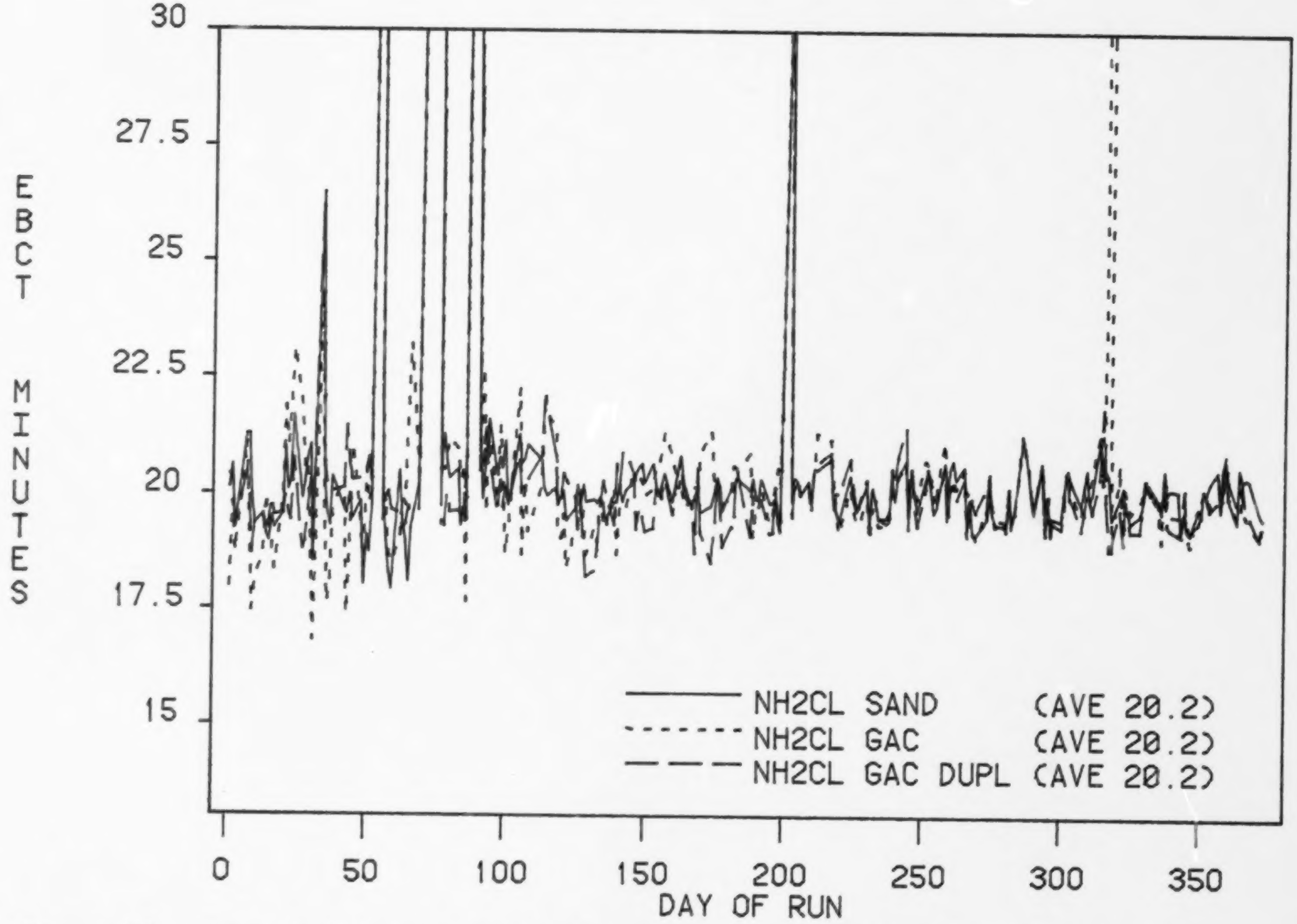


Figure 11. Empty Bed Contact Times Observed for the Chloramine Process Stream.

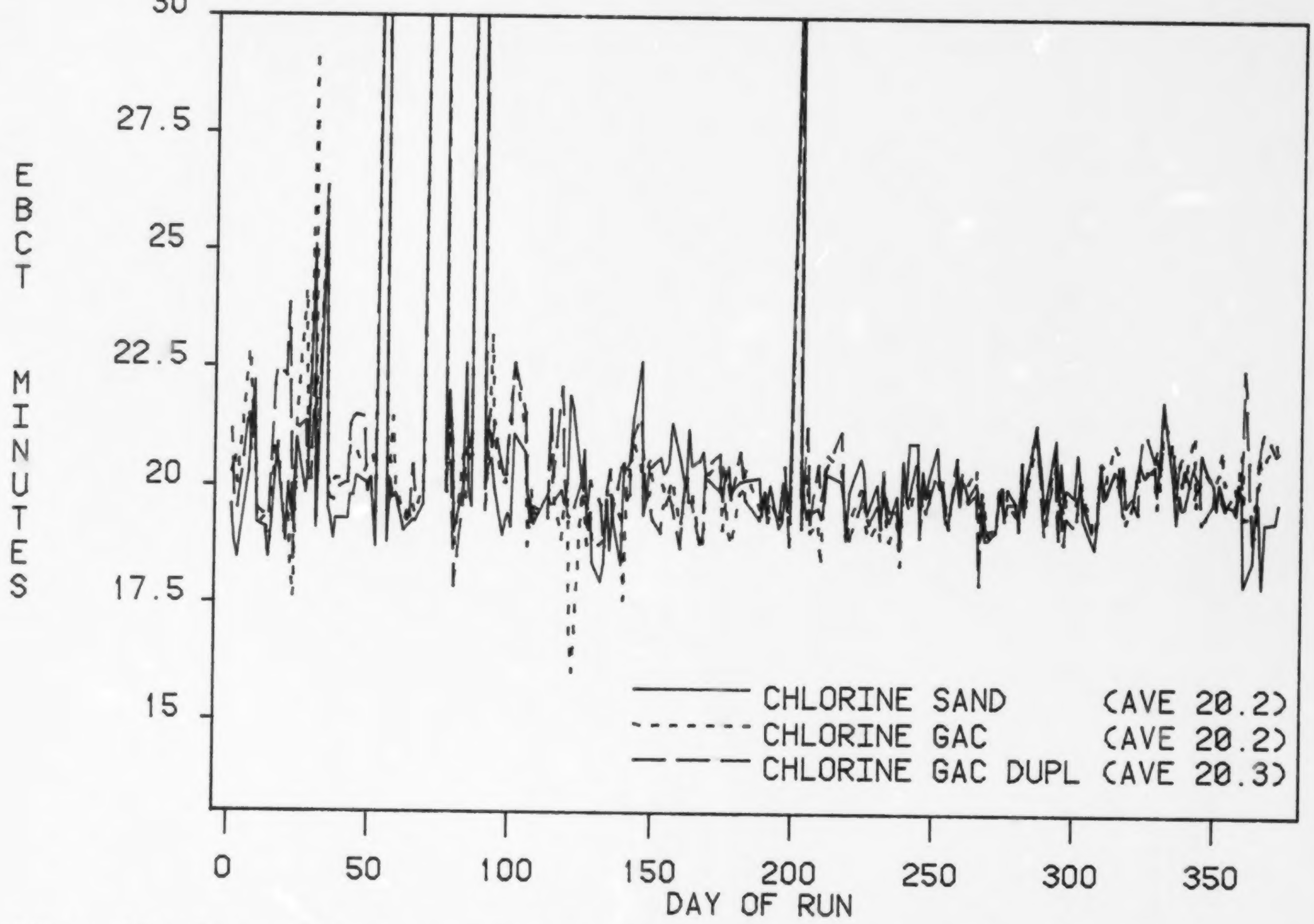


Figure 12. Empty Bed Contact Times Observed for the Chlorine Process Stream.

While some variations in EBCT were observed throughout the operational period, the relative variations of EBCT between pilot column locations were minimal as indicated in these figures and by the average EBCTs observed for each pilot column. The average EBCTs of the sand columns ranged between 20.1 and 20.9 minutes while those of the GAC columns ranged between 20.1 and 20.4 minutes. Because essentially the same EBCTs were observed for all locations, the analytical data presented in the later sections of this report are considered to be directly comparable. That is to say that those differences observed are attributable directly to the disinfectants used and not to differences in operational conditions such as EBCT.

During backwashing operations there was no sand lost from any of the sand columns and essentially no GAC lost from the GAC columns except for the nondisinfected GAC column and the ozone GAC duplicate column. Twenty six percent or 22 in. of GAC was lost from the nondisinfected GAC column on day 212 while 6% or 5 in. of GAC was lost from the ozone GAC duplicate column on day 309. No changes in effluent water quality were observed for any parameter for either of these locations after this loss of GAC indicating that this portion of each column had become saturated for those parameters monitored prior to the GAC being lost. For this reason all EBCTs indicated for those locations after this time do not reflect the change in GAC volume and were derived from the original GAC volumes of these two columns.

CHEMICAL OPERATING CONDITIONS

The average water quality of nondisinfected water entering the pilot column system after pressure sand filtration is shown in Table 16. After the addition of the various disinfectants, no significant changes in pH were observed which were greater than 0.1 pH units. The levels of pH for the chlorine dioxide and chlorine process streams were approximately 0.1 pH units below that of the other locations. The average thirty minute demands of each disinfectant determined during the operational period are compared in Table 17 along with their respective average process stream disinfectant residuals. With the exception of the ozone demand, these demands were determined by the difference of thirty minute residual readings of the various disinfectants applied at the same dosages to deionized water and nondisinfected influent water. The ozone demand was determined by measuring the difference in the concentration of ozone in the gas entering into and exiting from the ozone contact chamber and subtracting the ozone residual after making the appropriate corrections for gas and water flows through the contactor. The highest demands were observed for ozone and chlorine with the chlorine dioxide demand being considerably lower at 0.9 mg/l as ClO_2. The thirty minute chloramine demand, on the other hand, was essentially zero. While some demand was observed in the chloramine process stream

TABLE 16: AVERAGE WATER QUALITY OF NONDISINFECTED INFLUENT WATER TO THE PILOT COLUMN SYSTEM AFTER PRESSURE SAND FILTRATION

carbonates (mg/l)	0
bicarbonates (mg/l)	104
hydroxides (mg/l)	0
pH	7.5
total hardness (mg/l)	151
calcium (mg/l)	41
chlorides (mg/l)	27
turbidity (NTU)	0.38
temperature (°C)	17.5

TABLE 17: AVERAGE THIRTY MINUTE DISINFECTANT DEMANDS AND RESIDUALS

DISINFECTANT	AVERAGE 30 MINUTES DISINFECTANT DEMAND DETERMINATIONS (mg/l)	PROCESS STREAM AVERAGE DISINFECTANT CONTACT TIME (min)	PROCESS STREAM AVERAGE DISINFECTANT RESIDUALS (mg/l)
ozone	2.0 as O_3	31.7	0.5 as O_3
chlorine dioxide	0.9 as ClO_2	32.1	0.5 as ClO_2
monochloramine	0.0 as NH_2Cl	31.4	2.1 as NH_2Cl
chlorine	1.9 as Cl_2	31.8	1.0 as Cl_2

as will be indicated by TOX and trihalomethane formation in subsequent sections, the majority of this demand was attributable to the temporary presence of free chlorine which resulted from a pulsed ammonia feed as previously indicated in an earlier section.

A profile of the thirty minute residuals for each disinfectant as well as that for any associated disinfection products over the one year operational period are presented in Figures 13-17 while the averages of these data are compared in Table 18. The thirty minute ozone residual averaged 0.5 mg/l as O_3 with that for chlorine dioxide also averaging 0.5 mg/l as ClO_2. The average thirty minute residual for chlorite was slightly higher than that of chlorine dioxide at 0.6 mg/l as ClO_2^-. Essentially all of this chlorite resulted from the reduction of chlorine dioxide during the thirty minute contact period. This was determined through the examination of the data generated by the chlorine dioxide demand analyses which were performed in a batch mode using deionized carbon filtered water and nondisinfected pilot column influent water. The average concentrations of chlorine dioxide constituents in deionized carbon filtered water were 1.5 mg/l ClO_2, 0.0 mg/l ClO_2^-, 0.2 mg/l Cl_2, 0.1 mg/l NH_2Cl, and 0.1 mg/l $NHCl_2$. Those residuals observed after thirty minutes of contact time with the influent water of the pilot column system were 0.7 mg/l ClO_2, 0.6 mg/l ClO_2^-, 0.1 mg/l Cl_2, 0.2 mg/l NH_2Cl, and 0.1 mg/l $NHCl_2$. As mentioned earlier, comparison of these data show an average chlorine dioxide demand of 0.9 mg/l as ClO_2. These data further indicate that of this 0.9 mg/l ClO_2 demand, 0.6 mg/l or 67% was reduced to chlorite. According to White[2] this reduction to chlorite is generally accepted as the predominant reaction of chlorine dioxide in water treatment. The results indicated for the demand analyses would appear to be quite typical of those of the chlorine dioxide process stream since the average thirty minute residual concentrations for ClO_2^-, Cl_2, NH_2Cl, and $NHCl_2$ of the demand analyses were identical to those observed for the chlorine dioxide process stream during the operational period as indicated in Table 18. However, it is difficult to ascertain whether or not the low levels observed for Cl_2, NH_2Cl, and $NHCl_2$ were due to the actual presence of these constituents or to titration error in the form of endpoint fade back as one drop of titrant was equivalent to 0.05 mg/l Cl_2 for the demand determinations and to 0.1 mg/l for the residual measurements which occurred during the operational period. While no chlorate measurements were performed during the course of this study because the analytical method used did not respond to chlorate, the 96% yield observed for the chlorine dioxide reaction suggests indirectly that no detectable chlorate was formed as has been shown by E. M. AIETA etal[5]. However, this chlorine dioxide yield existed for optimum flow conditions of all reactants into the generator. Since several pump malfunctions occurred in the chlorine dioxide generating system causing flow rate irregularities, it is likely that some chlorate was formed on an intermittant basis.

The thirty minute monochloramine residual averaged 2.1 mg/l as NH_2Cl or 1.4 mg/l as Cl_2. A dichloramine residual was also observed averaging 0.4 mg/l as $NHCl_2$. This formation of

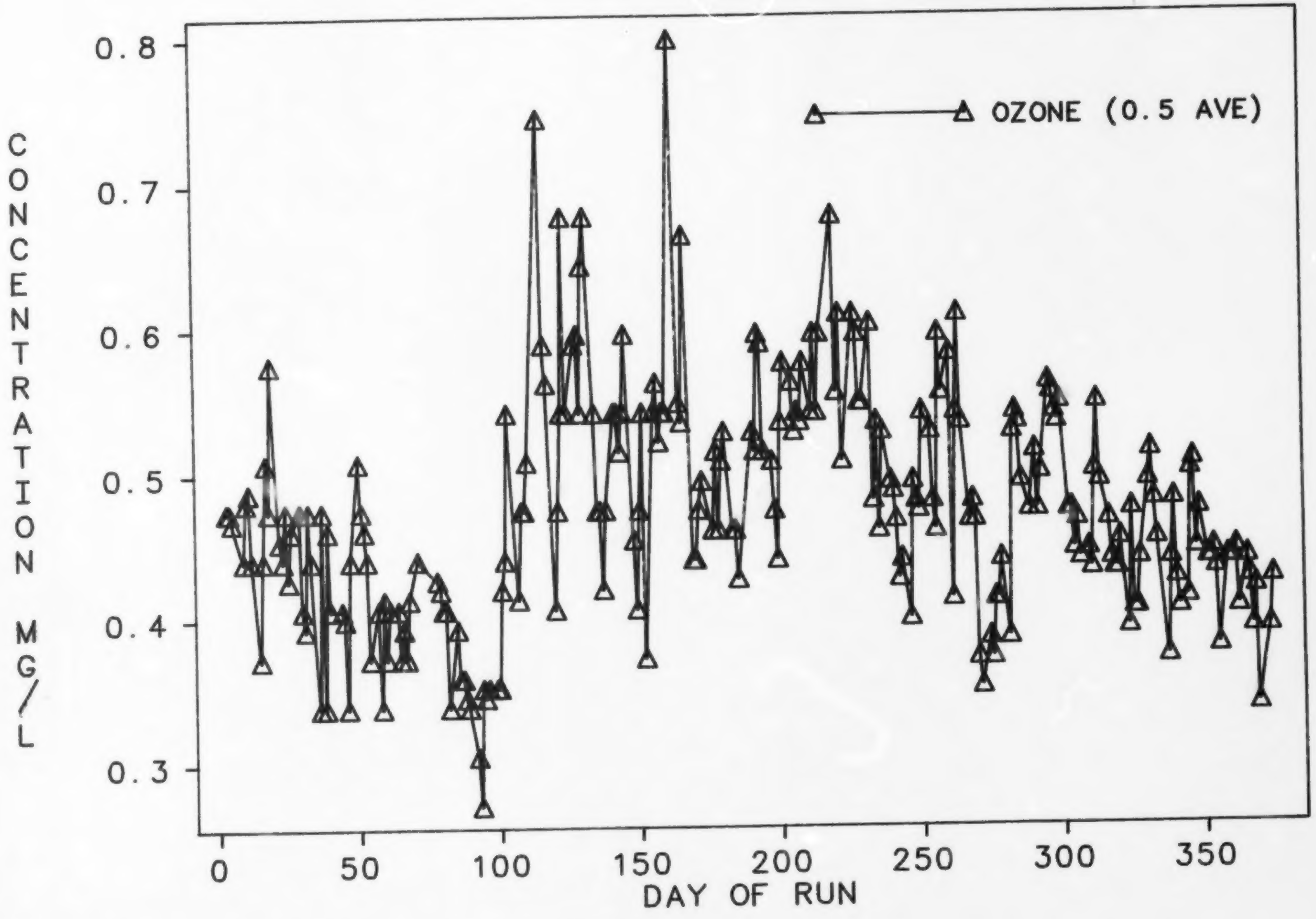


Figure 13. Ozone Residuals After 30 Minutes of Contact Time.

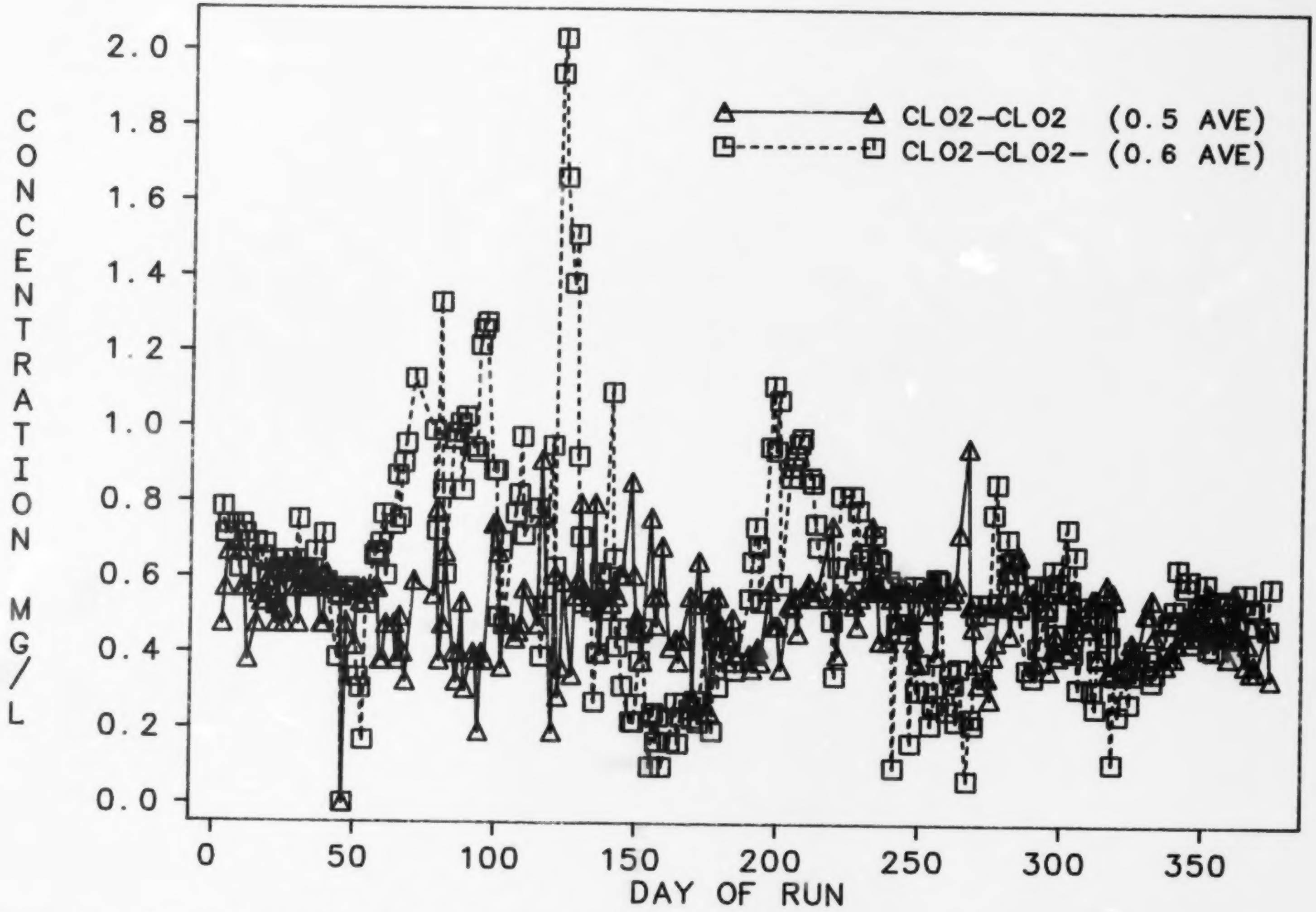


Figure 14. Chlorine Dioxide and Chlorite Residuals After 30 Minutes of Contact Time.

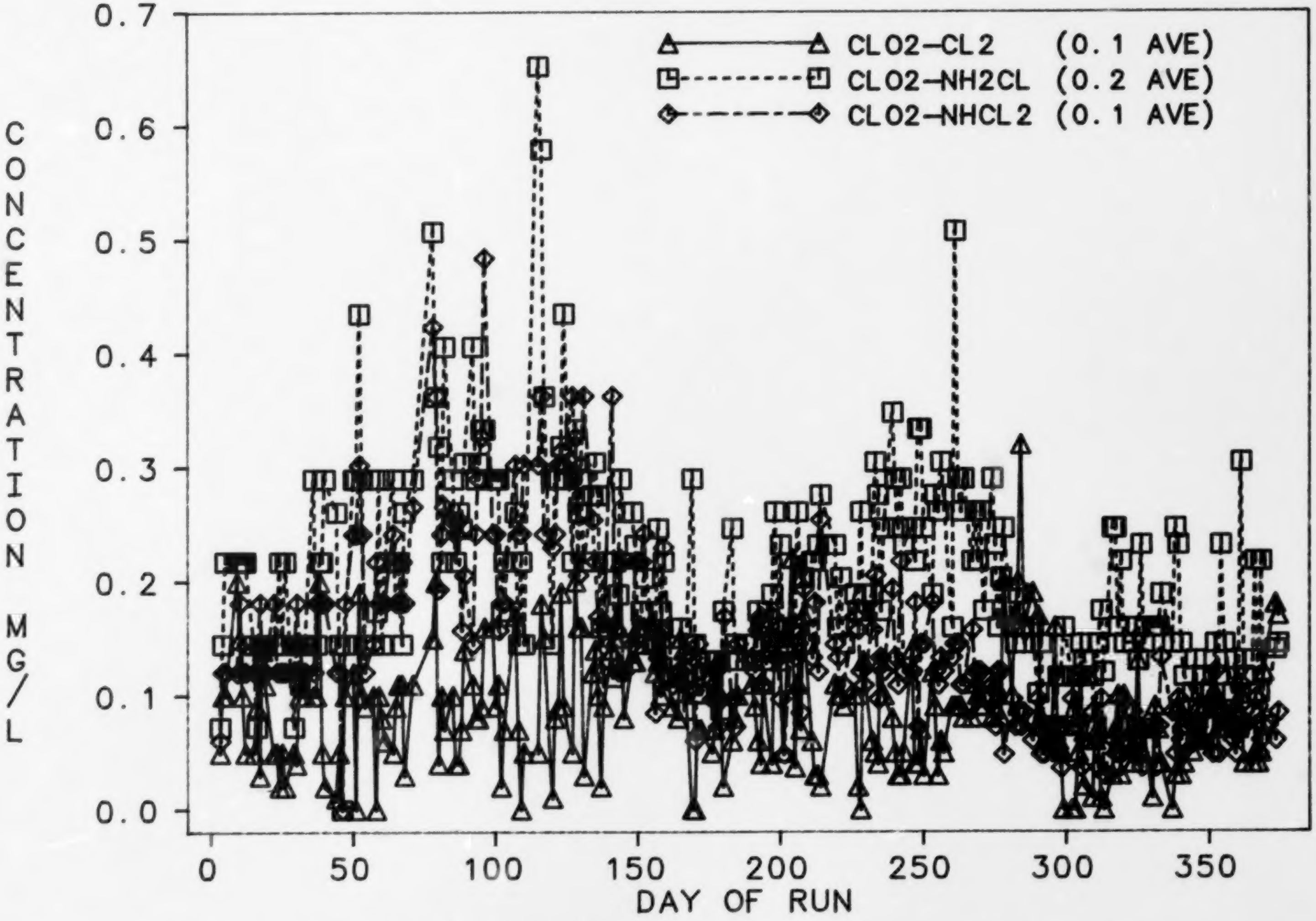


Figure 15. Free Chlorine, Monochloramine, and Dichloramine Residuals After 30 Minutes of Contact Time--Chlorine Dioxide System.

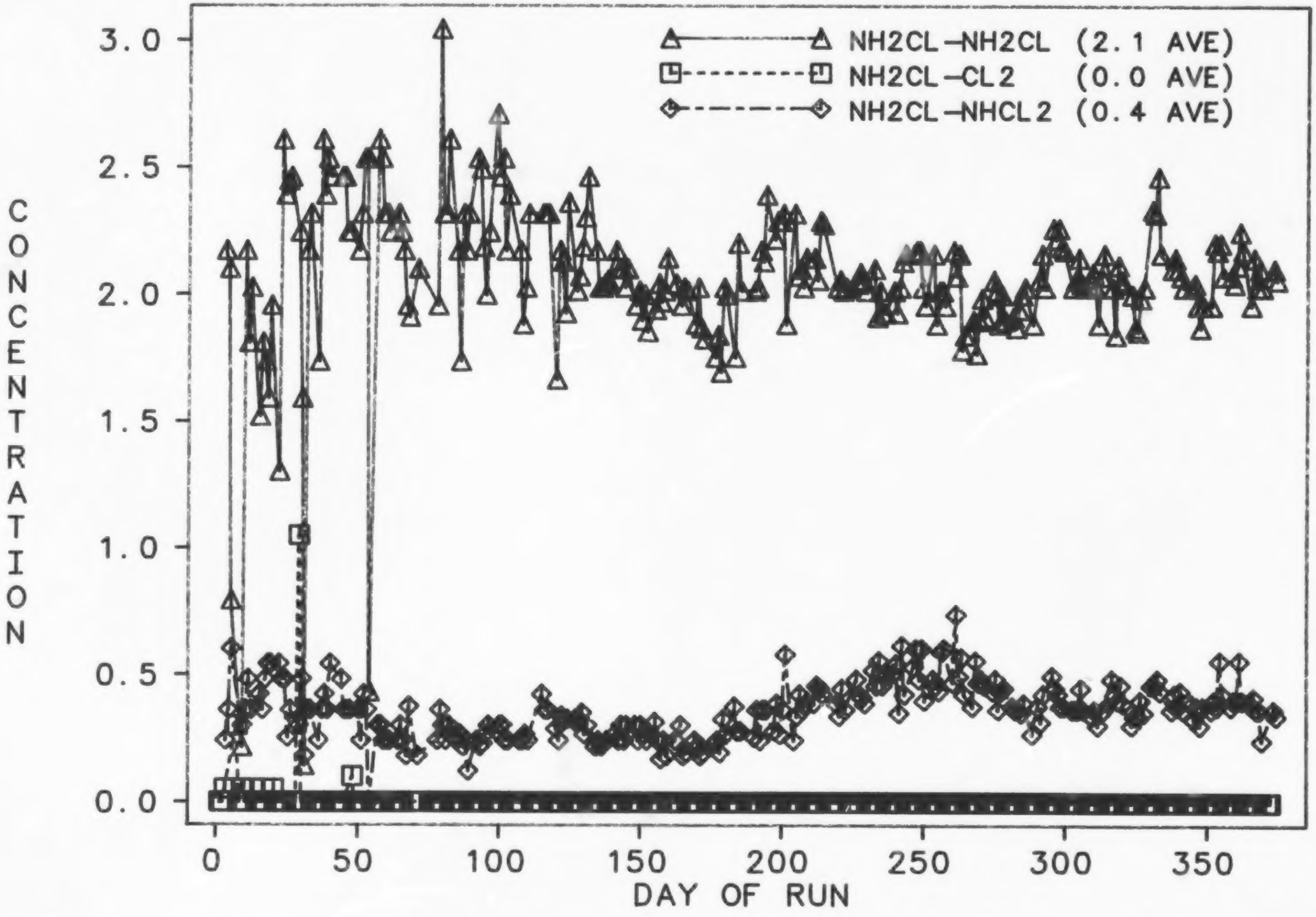


Figure 16. Free Chlorine, Monochloramine, and Dichloramine Residuals After 30 Minutes of Contact Time--Chloramine System.

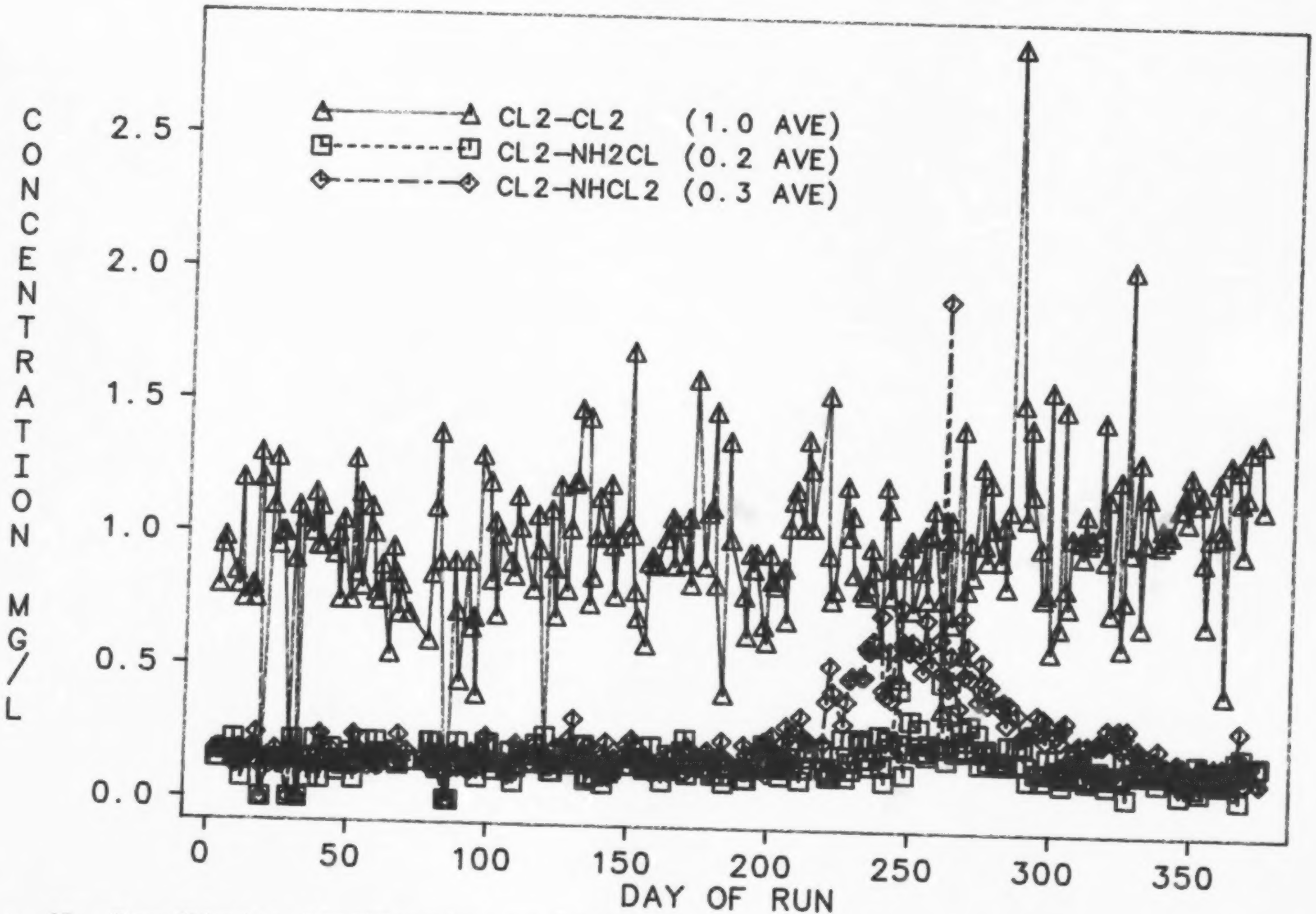


Figure 17. Free Chlorine, Monochloramine, and Dichloramine Residuals After 30 Minutes of Contact Time--Chlorine System.

TABLE 18: COMPARISON OF AVERAGE THIRTY MINUTE DISINFECTANT RESIDUALS OF EACH DISINFECTANT STREAM

PROCESS STREAM	DISINFECTANT CONSTITUENTS	AVERAGE THIRTY MINUTE RESIDUAL, mg/l
ozone	ozone	0.5 as O_3 (0.7 as Cl_2)
chlorine dioxide	chlorite	0.6 as ClO_2^- (1.3 as Cl_2)
	chlorine dioxide	0.5 as ClO_2 (1.3 as Cl_2)
	monochloramine	0.2 as NH_2Cl (0.1 as Cl_2)
	dichloramine	0.1 as $NHCl_2$ (0.1 as Cl_2)
	chlorine	0.1 as Cl_2
chloramine	monochloramine	2.1 as NH_2Cl (1.4 as Cl_2)
	dichloramine	0.4 as $NHCl_2$ (0.3 as Cl_2)
	chlorine	0.0 as Cl_2
chlorine	chlorine	1.0 as Cl_2
	dichloramine	0.3 as $NHCl_2$ (0.2 as Cl_2)
	monochloramine	0.2 as NH_2Cl (0.1 as Cl_2)

dichloramine was attributable to the intermittant variations in the chlorine to ammonia ratio resulting from a pulsed ammonia feed which was indicated in an earlier section. The fact that no dichloramine was observed in any of the demand analyses using nondisinfected pilot column influent water supports this assumption. Also, no dichloramine was observed in the finished water of the water treatment plants which use monochloramine as the sole disinfectant.

The average thirty minute chlorine residual observed for the chlorine process stream was 1.0 mg/l as Cl_2 along with an average monochloramine residual of 0.2 mg/l as NH_2Cl and an average dichloramine residual of 0.3 mg/l as $NHCl_2$. This generation of chloramines was due to the presence of naturally occuring ammonia which averaged from 0.1 - 0.2 mg/l of ammonia nitrogen. As indicated in Figure 17, the dichloramine residual rose from a level of 0.2 mg/l on day 200 to a maximum of 0.6 mg/l on day 260 followed by a gradual decrease back down to 0.2 mg/l on day 320.

This change in dichloramine concentration correlated quite well with a decrease in nondisinfected water temperature below 10°C as indicated in Figure 18. Further investigation showed that this increase in dichloramine was indeed attributable to low water temperature. Aliquots of the same water sample were chlorinated a 4°C and at room temperature. Those chlorinated at 4°C exhibited this higher dichloramine concentration while those chlorinated at room temperature did not.

Intermittant observations of the disinfectant residuals in the effluent of the GAC columns indicated that any remaining residuals were removed by the GAC. Similiar observations showed that ozone was completely dissipated across the ozone sand column while an approximate reduction of 0.2 mg/l of disinfectant residual was observed across the sand columns of the chlorine dioxide, chloramine, and chlorine process streams. In addition, approximately 0.5 mg/l of monochloramine was converted to dichloramine across the chloramine sand column.

BACTERIOLOGICAL CONDITIONS

HETEROTROPHIC PLATE COUNT --

The geometric means for the heterotrophic plate count (HPC) of each sampling location in each process stream are presented in Figure 19. After thirty minutes of disinfectant contact time, ozone was observed to have exhibited the highest level of disinfection with chlorine dioxide and chlorine close behind while chloramine was somewhat less effective. However, after filtration through the sand columns, chlorine dioxide, chlorine, and chloramine became equally effective. On the other hand, as ozonated water passed through the sand column the geometric mean for the HPC rose from 8 CFU/ml to 4594 CFU/ml indicating what might be considered a biologically activated sand column. The HPC levels in the effluent of each sand column are compared in Figure 20. It is interesting to note that while the geometric means for the HPC increased across the sand columns for all of the disinfected process streams, that for the nondisinfected process stream significantly decreased. Because each disinfectant was rendered ineffective in the first portion of each GAC column, the geometric mean of the heterotrophic plate count in the effluent of each disinfected GAC column increased dramatically back to a level similiar to that observed for the nondisinfected influent water of the pilot column system. One may surmise that the geometric means for heterotrophic plate count in the effluent of the ozone GAC columns were significantly lower than that observed for the ozone sand column because of the dissimiliarities of the pore structure of the two medias which might allow more bacteria to be dislodged from the sand particles. However, this was not evident since the geometric

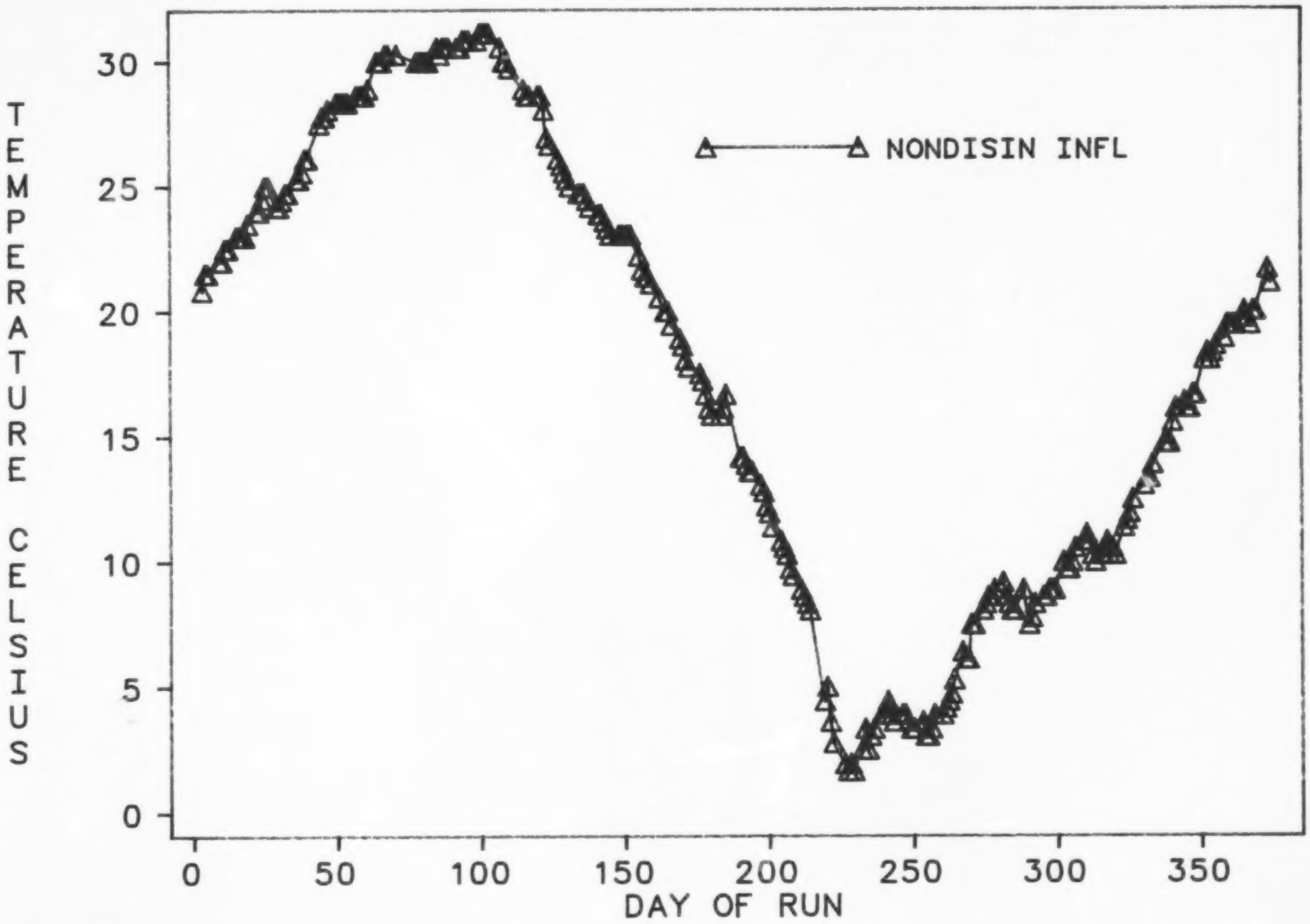


Figure 18. Temperature of the Nondisinfected Influent Water Entering the Pilot Column System.

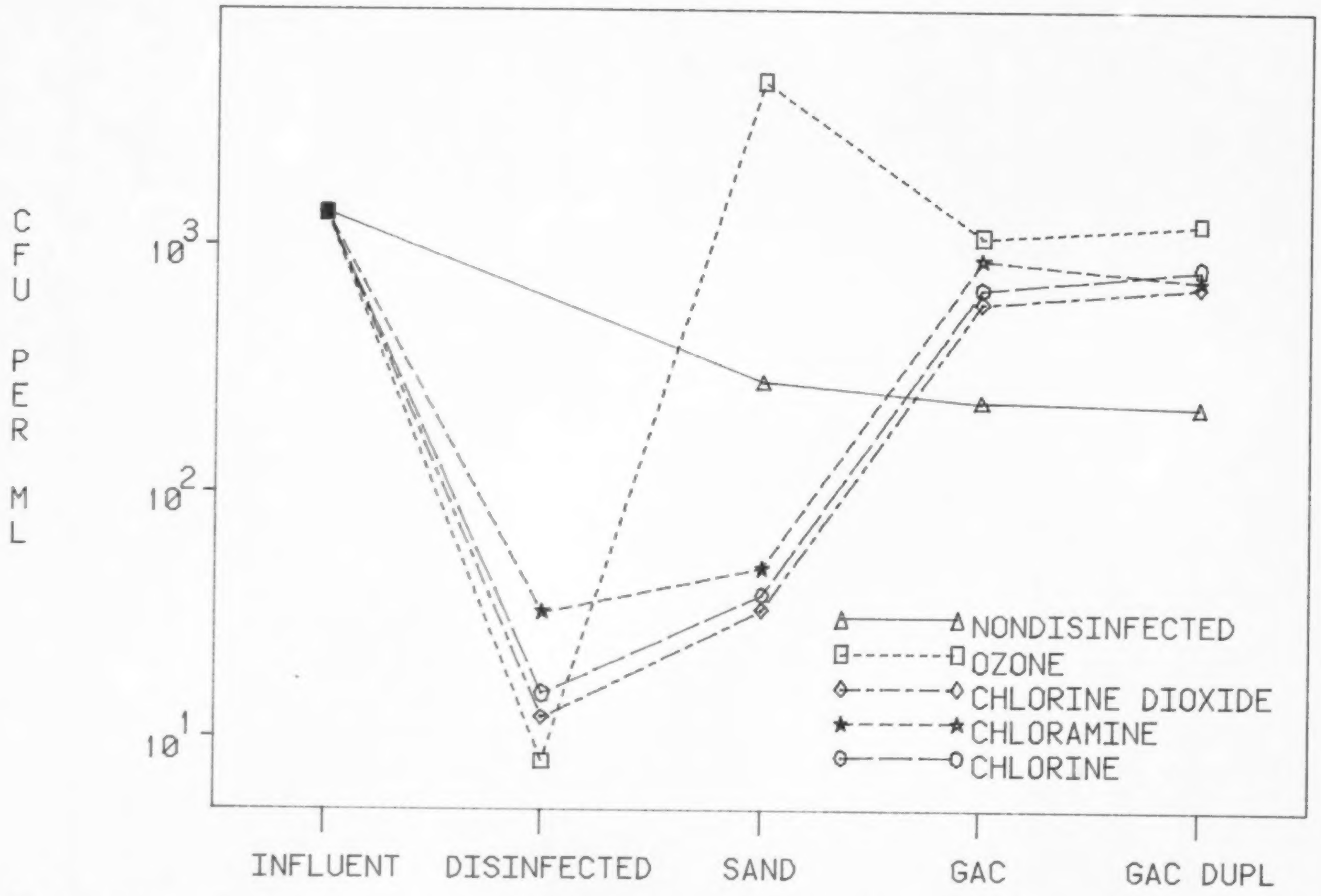


Figure 19. Comparison of the Average Geometric Means of the Heterotrophic Plate Count for the Influent and Effluent Locations of each Process Stream.

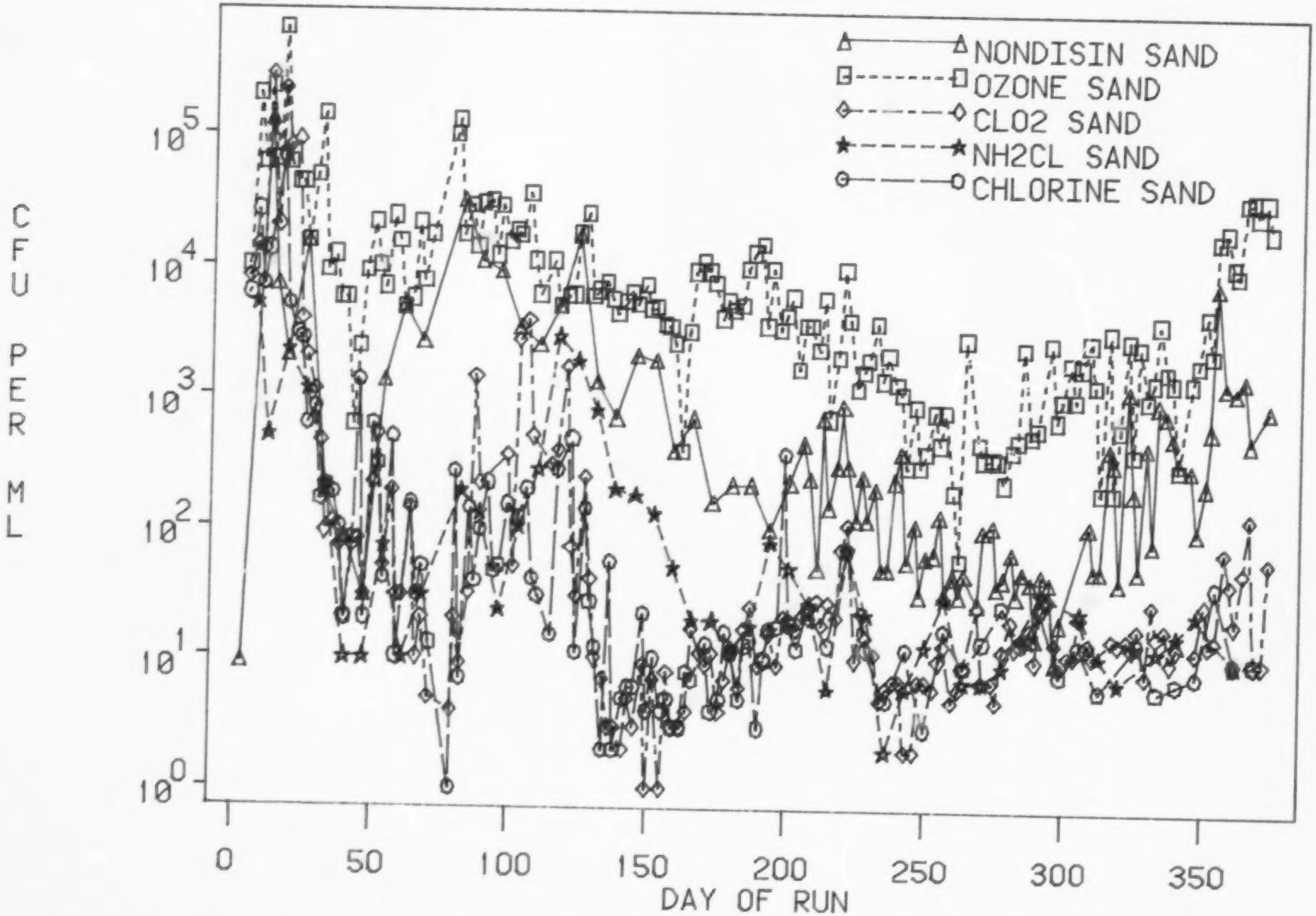


Figure 20. Comparison of the Heterotrophic Plate Count in the Effluents of each Sand Column.

means observed for the nondisinfected sand and GAC columns were essentially the same. The geometric means of heterotrophic plate count in the effluents of the nondisinfected GAC columns were also significantly lower than those observed for the GAC columns of each disinfected process stream. No explanation for these lower heterotrophic plate count levels was apparent other than to surmise that suppression by the applied disinfectants produced a rapid regrowth response which was greater than normal once the disinfectant was rendered inactive by the upper portion of each GAC column.

DISSOLVED OXYGEN--

Dissolved oxygen (DO) is presented in this section because it is an indicator of aerobic biological activity. The average concentrations of DO observed in each step of each process stream are presented in Figure 21. As expected, the effluent from the ozone contactor and the ozone sand column contained higher DO levels than did those of the other process streams. This increase was not attributable to ozone as the oxygen probe used did not respond to ozone. The levels of DO observed in the effluents of the GAC columns were varied as were the reductions of DO across each GAC column as indicated in Figure 22. The highest consumption of DO was observed for the ozone and chloramine GAC columns at 3.2 - 3.4 mg/l followed by the nondisinfected GAC columns at 2.4 mg/l, the chlorine GAC columns at 1.8 mg/l, and the chlorine dioxide GAC columns at 1.4 mg/l. The consumptions of DO across the sand and GAC columns of each process stream, for the most part, do not correlate with the geometric means of the HPC observed. While the highest consumptions of DO were observed for the ozone and chloramine GAC columns which also observed the highest effluent levels of HPC, the nondisinfected GAC columns exhibited the lowest HPC levels while also exhibiting the third highest DO consumption. This difference is attributed to changes in the distribution of bacterial species present in each process stream which were brought about by the various disinfectants applied. For example, total coliforms which were not detected by API speciation of HPC isolates, were present in the nondisinfected system but were not present to any extent in any of the disinfected systems. This suggests that other bacteria may also be present in the nondisinfected process stream which are undetectable by HPC but which would account for the consumption of DO. Thus, it was indicated that DO may be a better indicator of total biological activity than is HPC.

Another anomaly was that the DO consumption for the ozone sand column was much less than that of the ozone GAC columns, but the effluent of the ozone sand column contained higher HPC levels. This was attributable to the adsorption of DO by the GAC

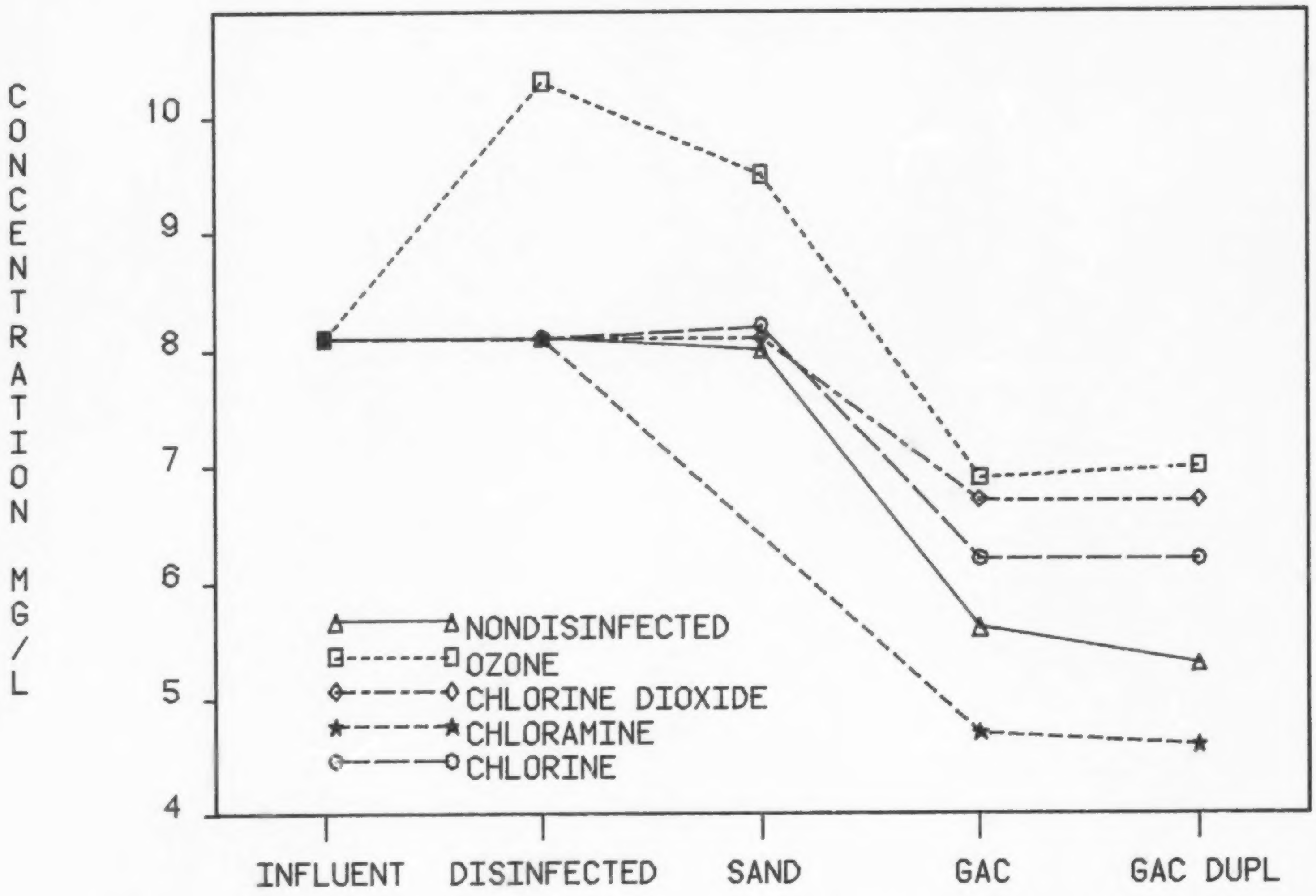


Figure 21. Comparison of the Average Dissolved Oxygen Levels in the Influent and Effluent of each Process Stream.

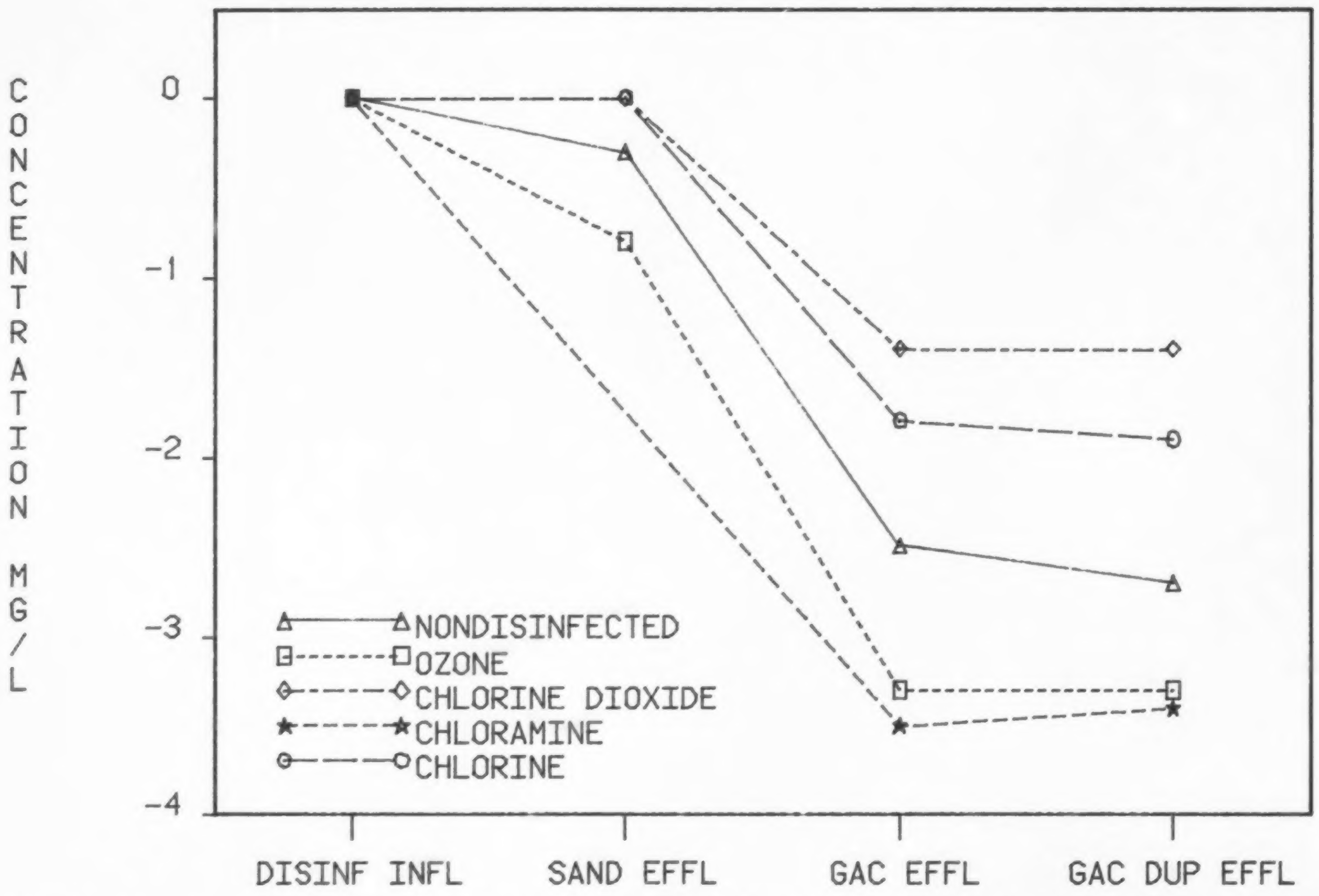


Figure 22. Comparison of the Average Change in Dissolved Oxygen in the Influent and Effluent of each Process Stream.

column and would similiarly explain the higher DO consumptions observed for the nondisinfected GAC columns as compared to the nondisinfected sand column with the same effluent HPCs having been observed for each of these columns. Thus, DO consumption can be used to compare the relative levels of biological activity between GAC columns but not their absolute biological activity for comparison to the sand columns due to the unknown level of adsorption of DO by the GAC column.

HETEROTROPHIC PLATE COUNT SPECIATION--

In a effort to determine what types of gram negative bacteria were prevalent in the influent and effluent of each pilot column, bacterial colonies from each heterotrophic plate were streaked for isolation on nutrient agar and identified via the API 20E enterobacteriaceae system. From two to five colonies were picked from each heterotrophic plate depending upon the visual differences observed between colonies. While this was by no means an accurate method for identifing their respective populations, it was felt that this procedure would yield base line data on the possible types of gram negative bacteria which might be present in the effluents of these systems while at the same time maintaining the bacteriological workload at a reasonable level.

Those bacteria observed in the influent and effluent waters of the sand, GAC, and GAC duplicate columns along with their frequency of observation are presented in Tables 19-22. Examination of these data indicates that the majority of the colonies picked from the heterotrophic plates were gram positive. Also a considerably high frequency of no regrowth occurred for the isolation streak. The most frequently observed gram negative bacteria were *Pseudomonas*, *Alcaligenes*, *Moraxella*, and *Acinetobacter calcoaceticas*. A few gram negative bacteria were observed which could not be indentified.

TOTAL COLIFORM--

The number of positive samples and the average plate counts observed for total coliform from each sampling location of the pilot column system are presented in Table 23. Those positive samples observed in the influents and the sand column effluents of the disinfected process streams are attributable to a loss or reduction in disinfectant feed due to an equipment malfunction or to sample contamination. Also, the majority of the positive samples observed in the effluents of the GAC and GAC duplicate columns occurred at the beginning of the operational period and were also associated with disinfectant feeding equipment malfunctions. Very few positive samples occurred in the latter

TABLE 19: FREQUENCY OF OCCURRANCE OF VARIOUS GRAM NEGATIVE BACTERIA FOR THE INFLUENT WATER TO EACH PILOT COLUMN OF EACH PROCESS STREAM

BACTERIA	NONDISIN	OZONE	CLO_2	NH_2Cl	CHLORINE
Achromobacter xylosidans	--	--	--	--	--
Acinetobacter calcoaceticus	7	--	--	3	1
Aeromonas hydrophila	4	--	--	--	1
Agrobacterium radiobacter	1	1	--	--	--
Alcaligenes	11	2	--	5	1
CDC enteric II	--	--	--	--	--
CDC group II F	2	--	--	--	--
CDC group III F	--	--	--	--	--
CDC group IV E	--	--	--	--	--
CDC group V E-2	--	1	--	--	--
Chromobacterium	1	--	--	--	--
Citrobacter freundii	--	--	--	--	--
Cytophaga	--	--	--	--	--
Enterobacter agglomerans	--	--	--	--	--
Enterobacter cloacae	--	--	--	--	--
Flavobacterium breve	--	--	--	--	--
Flavobacterium meningosepicum	1	--	1	2	--
Flavobacterium odoratum	2	--	1	1	--
Moraxella	7	2	1	11	5
Pasteurella	1	--	--	--	--
Pasteurella actinobacter	2	--	--	2	1
Plesiomonas shigelloides	--	--	--	--	--
Pseudomonas	12	3	2	6	2
Pseudomonas fluorescens	--	1	--	1	--
Pseudomonas maltophilia	2	--	2	1	--
Pseudomonas paucimobilis	1	1	4	4	1
Pseudomonas stutzeri	--	--	--	--	--
Serratia liquefaciens	--	--	--	--	--
Serratia rubidaea	--	--	--	--	--
Shigella	--	--	--	--	--
Shigella dysenteriae	--	--	--	--	--
Vibrio parahaemolyticus	--	--	--	--	--
Gram positive	25	34	40	34	43
Unknown	--	--	--	1	1
No regrowth	15	14	9	13	6

TABLE 20: FREQUENCY OF OCCURRANCE OF VARIOUS GRAM NEGATIVE BACTERIA FOR THE EFFLUENT OF THE SAND COLUMNS OF EACH PROCESS STREAM

BACTERIA	NONDISIN	OZONE	CLO_2	NH_2Cl	CHLORINE
Achromobacter xylosidans	4	10	4	3	1
Acinetobacter calcoaceticus	1	--	--	--	--
Aeromonas hydrophila	--	1	1	1	--
Agrobacterium radiobacter	11	16	2	3	1
Alcaligenes	--	--	--	--	--
CDC enteric II	--	2	--	--	--
CDC group II F	--	--	1	--	--
CDC group III F	--	--	--	--	--
CDC group IV E	--	--	--	--	--
CDC group V E-2	--	--	--	--	--
Chromobacterium	--	--	--	--	--
Citrobacter freundii	--	--	--	--	--
Cytophaga	--	--	--	--	--
Enterobacter agglomerans	--	--	--	--	--
Enterobacter cloacae	--	--	--	--	--
Flavobacterium breve	--	--	--	--	--
Flavobacterium memingosepicum	1	4	--	--	--
Flavobacterium odoratum	7	15	1	2	3
Moraxella	1	--	--	--	--
Pasteurella	--	2	--	--	--
Pasteurella actinobacter	--	--	--	--	--
Plesiomonas shigelloides	9	17	1	1	2
Pseudomonas	1	--	--	--	--
Pseudomonas fluorescens	1	1	1	--	1
Psedomonas maltophilia	4	2	2	1	--
Pseudomonas paucimobilis	1	2	--	--	1
Pseudomonas stutzeri	--	--	--	--	--
Serratia liquefaciens	--	--	--	--	--
Serratia rubidaea	--	--	--	--	--
Shigella	--	--	--	--	--
Shigella dysenteriae	--	--	--	--	--
Vibrio parahaemolyticus	--	--	--	--	--
Gram positive	21	17	40	20	30
Unknown	1	1	-	--	1
No regrowth	13	14	6	6	2

TABLE 21: FREQUENCY OF OCCURRANCE OF VARIOUS GRAM NEGATIVE BACTERIA FOR THE EFFLUENT OF THE GAC COLUMNS OF EACH PROCESS STREAM

BACTERIA	NONDISIN	OZONE	CLO_2	NH2Cl	CHLORINE
Achromobacter xylosidans	6	4	5	4	8
Acinetobacter calcoaceticus	2	1	--	--	--
Aeromonas hydrophila	--	--	--	--	--
Agrobacterium radiobacter	5	18	5	4	9
Alcaligenes	1	--	--	--	--
CDC enteric II	--	2	--	--	--
CDC group II F	--	--	--	--	--
CDC group III F	1	1	--	--	--
CDC group IV E	--	--	--	--	--
CDC group V E-2	--	--	--	--	--
Chromobacterium	--	--	--	1	1
Citrobacter freundii	--	--	1	--	--
Cytophaga	1	--	--	--	--
Enterobacter agglomerans	--	1	--	--	--
Enterobacter cloacae	--	--	--	1	--
Flavobacterium breve	--	2	--	--	1
Flavobacterium meningosepicum	1	--	5	--	1
Flavobacterium odoratum	4	9	4	7	6
Moraxella	2	--	--	--	--
Pasteurella	1	--	--	2	1
Pasteurella actinobacter	1	--	--	--	--
Plesiomonas shigelloides	10	14	14	14	10
Pseudomonas	--	--	--	--	--
Pseudomonas fluorescens	1	2	6	3	1
Pseudomonas maltophilia	1	1	1	1	--
Pseudomonas paucimobilis	1	1	--	--	--
Pseudomonas stutzeri	--	--	--	1	--
Serratia liquefaciens	1	--	--	--	--
Serratia rubidaea	--	--	--	--	--
Shigella	1	--	--	--	--
Shigella dysenteriae	1	--	--	--	--
Vibrio parahaemolyticus	1	--	--	--	--
Gram positive	25	20	29	22	21
Unknown	--	--	--	--	1
No regrowth	13	20	14	23	18

TABLE 22: FREQUENCY OF OCCURRANCE OF VARIOUS GRAM NEGATIVE BACTERIA FOR THE EFFLUENT OF THE GAC DUPLICATE COLUMNS OF EACH PROCESS STREAM

BACTERIA	NONDISIN	OZONE	CLO_2	NH_2Cl	CHLORINE
Achromobacter xylosidans	--	2	--	--	--
Acinetobacter calcoacetius	1	10	7	2	6
Aeromonas hydrophila	4	--	--	--	--
Agrobacterium radiobacter	--	1	--	1	--
Alcaligenes	11	10	7	4	4
CDC enteric II	--	--	--	--	--
CDC group II F	1	2	--	--	1
CDC group III F	--	--	--	--	--
CDC group IV E	--	--	--	--	--
CDC group V E-2	--	--	--	--	--
Chromobacterium	--	--	--	--	--
Citrobacter freundii	--	--	3	--	--
Cytophaga	--	--	--	--	--
Enterobacter agglomerans	--	--	--	--	--
Enterobacter cloacae	--	--	--	--	--
Flavobacterium breve	--	--	--	--	--
Flavobacterium meningosepicum	--	--	2	1	1
Flavobacterium odoratum	6	8	5	8	10
Moraxella	1	--	--	--	--
Pasteurella	1	1	--	2	1
Pasteurella actinobacter	--	--	--	--	--
Plesiomonas shigelloides	11	11	10	7	16
Pseudomonas	--	--	--	--	--
Pseudomonas fluorescens	--	2	2	2	1
Pseudomonas maltophilia	2	2	1	--	2
Pseudomonas paucimobilis	--	2	1	--	--
Pseudomonas stutzeri	--	--	--	--	--
Serratia liquefaciens	--	--	--	--	--
Serratia rubidaea	--	--	--	--	--
Shigella	--	--	--	1	--
Shigella dysenteriae	1	--	--	--	--
Vibrio parahaemolyticus	--	--	--	--	--
Gram positive	28	22	26	25	18
Unknown	1	1	1	4	--
No regrowth	14	19	17	23	19

TABLE 23: AVERAGE TOTAL COLIFORM DATA FOR EACH SAMPLING LOCATION OF THE PILOT COLUMN SYSTEM

	TOTAL COLIFORM (NO. OF POSITIVE SAMPLES/AVERAGE COUNT/100ml)				
	NONDISIN	OZONE	CHLORINE DIOXIDE	CHLORAMINE	CHLORINE
Influent	149/132	0/0	2/29	1/1	1/87
Sand effluent	91/29	1/1	2/24	0/0	1/95
GAC effluent	125/13	3/2	3/5	7/2	8/14
GAC duplicate effluent	127/11	0/0	5/4	4/1	11/9

part of the operational period [illegible] effluents of the GAC and GAC duplicate columns with all [illegible] coliform levels being at 3/100 ml or below. From these [illegible] it would appear that the coliform bacteria present did not proliferate to any great extent on the GAC columns once the disinfectants had been removed by the first portion of the GAC beds. In fact, total coliform counts decreased across the sand, GAC, and GAC duplicate columns of the nondisinfected process stream producing reductions of 72.5, 87.5 and 87.0 percent, respectively.

SECTION 7

RESULTS AND DISCUSSION

TOTAL ORGANIC CARBON (TOC)

The total organic carbon (TOC) levels in the effluent of the disinfectant contact chamber of each disinfectant stream after 30 minutes of disinfectant contact time are compared in Figure 23 to that of the influent of the nondisinfected stream which was also the influent of each disinfectant contact chamber. The TOC levels in each of these streams were quite similiar with average values of 3.33 mg/l for the nondisinfected stream, 3.04 mg/l for the ozone stream, 3.28 mg/l for the chlorine dioxide stream, 3.35 mg/l for the chloramine stream, and 3.27 mg/l for the chlorine stream. While it is difficult to observe any difference between the disinfectant streams relative to TOC removal in Figure 23 the average values obtained for each process stream indicate that the only significant reduction which occurred was that for the ozone stream. An average reduction of 0.3 mg/l of TOC resulted after 30 minutes of ozone contact with a final average ozone residual of 0.47 mg/l.

The TOC levels in the effluent of each control sand column of the various process streams are presented in Figure 24. Immediately apparent is a considerable reduction in TOC which occurred across the sand column of the ozone stream. The average TOC level in the effluent of the ozone sand column was 2.5 mg/l while those for all of the other process streams were equal to their influent values indicated earlier. The average reduction of TOC across the sand column was 0.5 mg/l. Thus, the total reduction in TOC observed for ozonation followed by sand filtration was 0.8 mg/l while that for the other process streams was essentially zero. The reduction in TOC across the ozone sand column can be attributed to increased biological activity as evidenced by the higher geometric mean of the heterotrophic plate count (HPC) observed in the effluent of this column of 4,594 CFU/ml, as compared to 278, 33, 49, and 38 CFU/ml which were observed in the effluents of the nondisinfected, chlorine dioxide, chloramine, and chlorine sand columns, respectively.

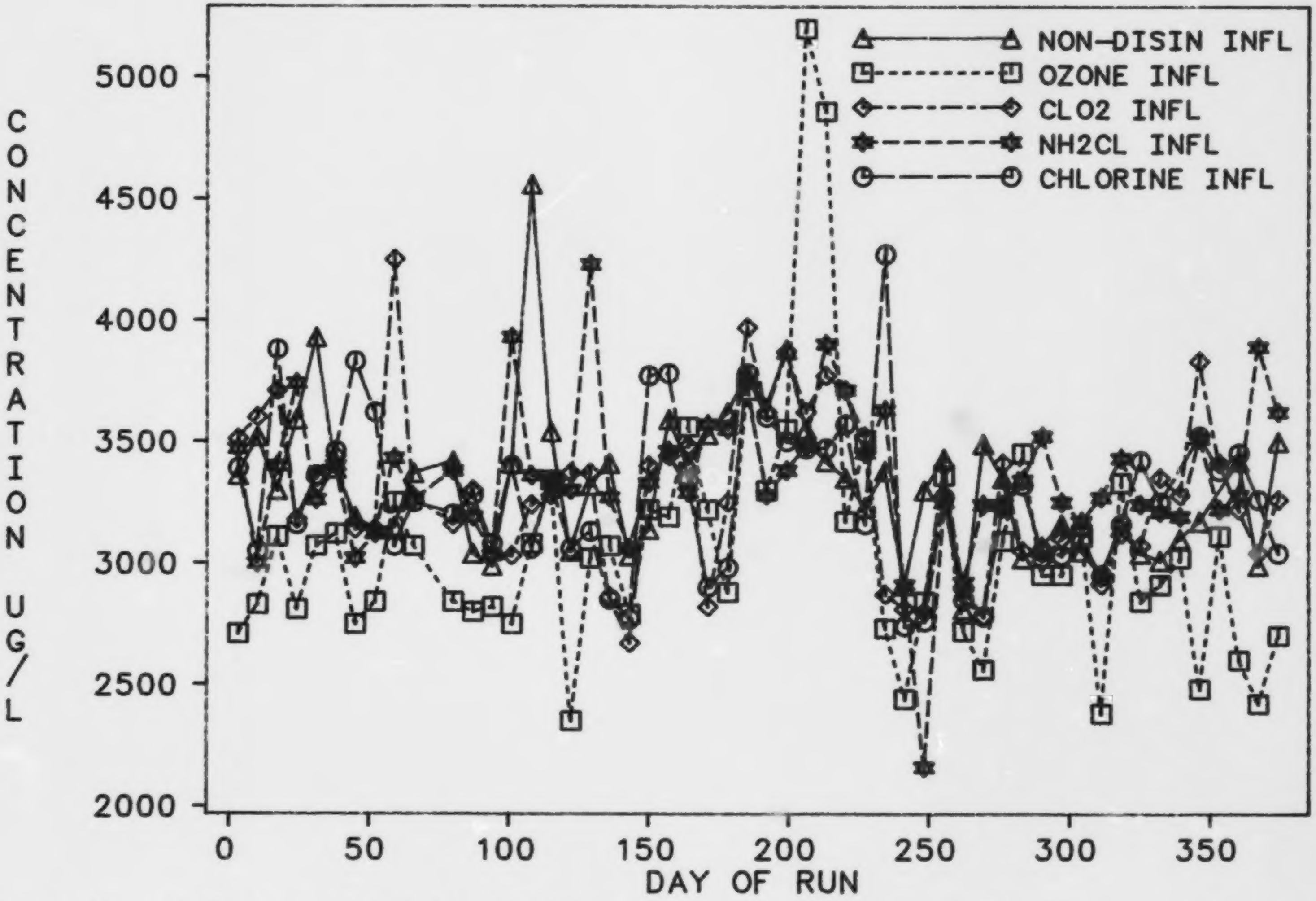


Figure 23. Comparison of the TOC Influent Levels for each Process Stream.

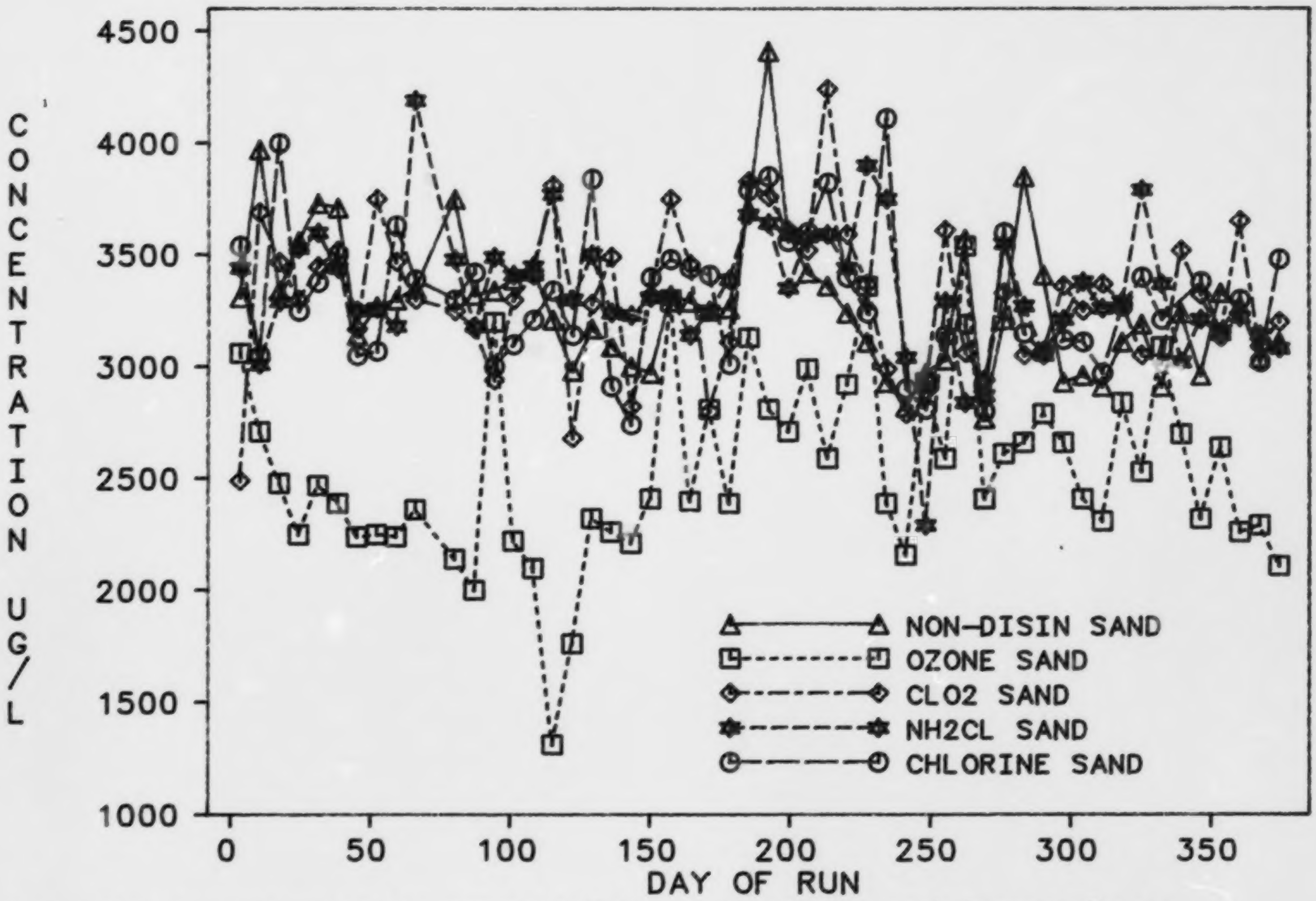


Figure 24. Comparison of the TOC Sand Effluent Levels for each Process Stream.

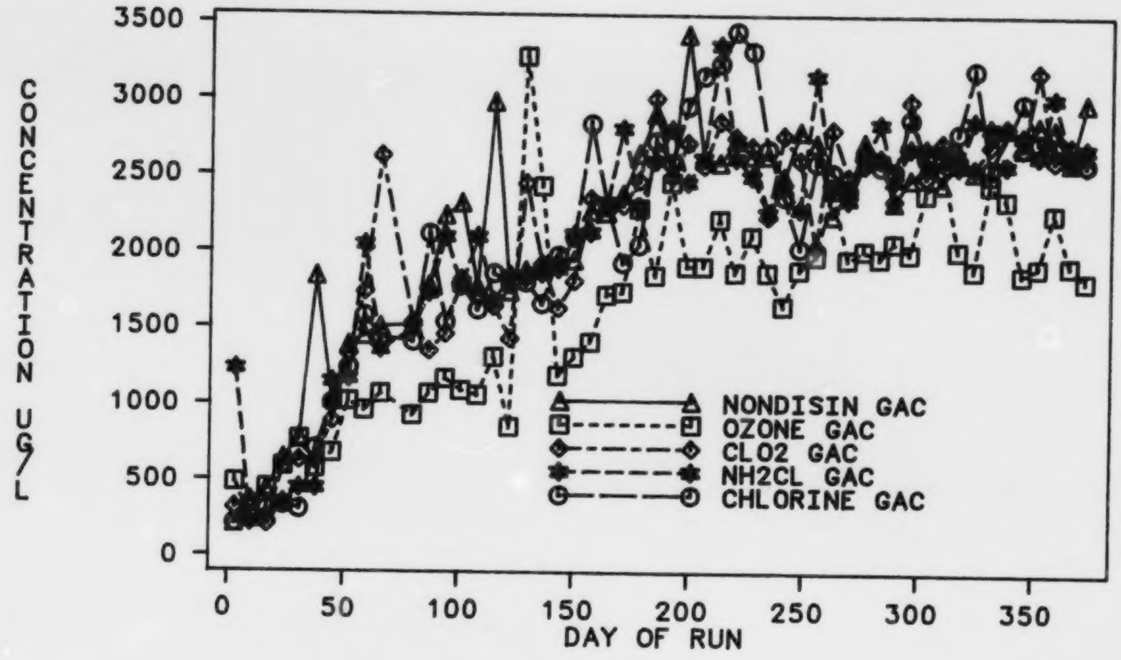
Similiarly, lower effluent TOC levels were observed for the GAC and GAC duplicate columns of the ozone process stream as compared to those observed for the other process streams as indicated in Figure 25. The average effluent concentrations of the ozone GAC columns were 0.5 mg/l lower than those of the other process streams. This lower average concentration was derived from a 0.3 mg/l lower average influent concentration in conjunction with a 0.2 mg/l greater average reduction across the GAC columns of the ozone stream as compared to that of the other process streams. The reductions in the levels of TOC across the GAC columns of each process stream are compared in Figure 26. The presence of increased biological activity on the GAC columns of the ozone stream as compared to those of the other process streams was not as evident as that for the control sand columns. The geometric means of effluent HPC observed for the GAC columns of each stream were 229 and 220 CFU/ml for the nondisinfected stream, 1083 and 1220 CFU/ml for the ozone stream, 583 and 583 CFU/ml for the chlorine dioxide stream, 872 and 720 CFU/ml for the chloramine system, and 664 and 804 CFU/ml for the chlorine stream. Although the differential in the geometric means of effluent HPC were not as great as that observed for the control sand columns, the highest levels of HPC were again observed in the effluent of the ozone GAC columns.

The breakthrough profiles of TOC through the GAC columns of each process stream are presented in Figures 27 - 31. These figures indicate that the GAC columns of each process stream reached a "steady state" condition on approximately day 180. The TOC level at which each GAC column reached the "steady state" condition was approximately 2.7 mg/l for all of the process streams except for the ozone stream which was approximately 2.2 mg/l. These figures further illustrate that essentially identical TOC data was observed for the GAC columns and the GAC duplicate columns of each process stream.

TOTAL ORGANIC HALIDE (TOX)

INSTANTANEOUS TOX --

As might be expected, the highest levels of TOX were observed in the chlorine stream with the lowest levels occurring in the ozone stream. The TOX levels produced in the influent water of each disinfectant process stream after 30 minutes of disinfectant contact time are compared to the influent of the nondisinfected stream in Figure 32. The average influent TOX levels observed for each process stream were 25 ug/l for the nondisinfected stream, 15 ug/l for the ozone stream, 85 ug/l for the chlorine dioxide stream, 117 ug/l for the chloramine stream, and 253 ug/l for the chlorine stream. Thus, the average levels of TOX produced by chlorine dioxide, chloramine, and chlorine after 30



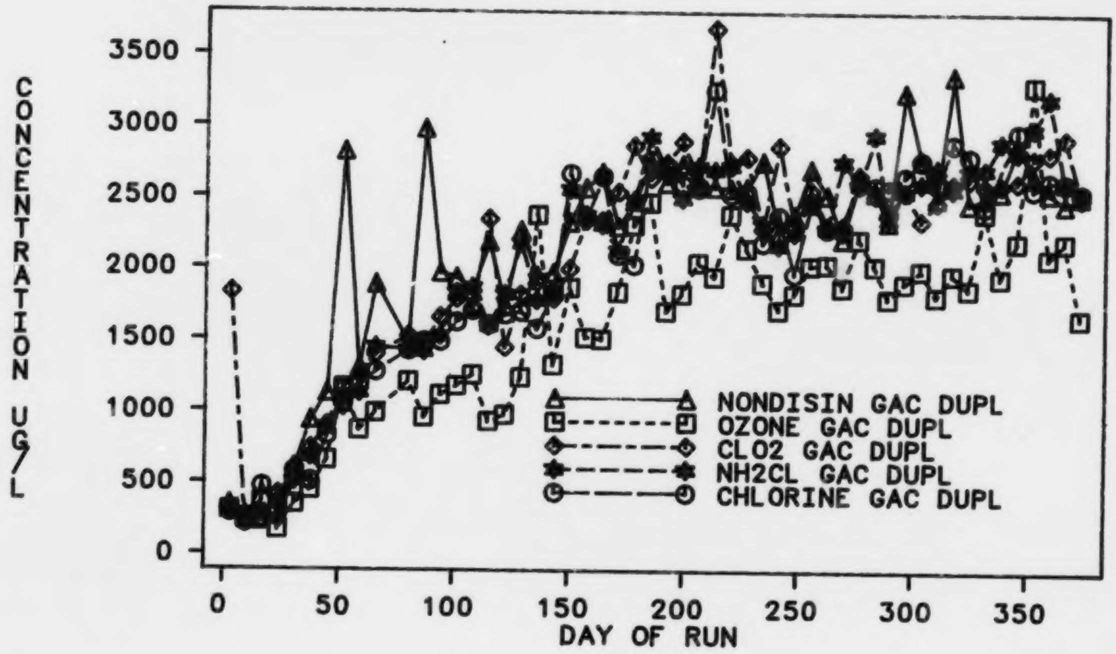


Figure 25. Comparison of the TOC GAC and GAC Duplicate Effluent Levels for Each Process Stream.

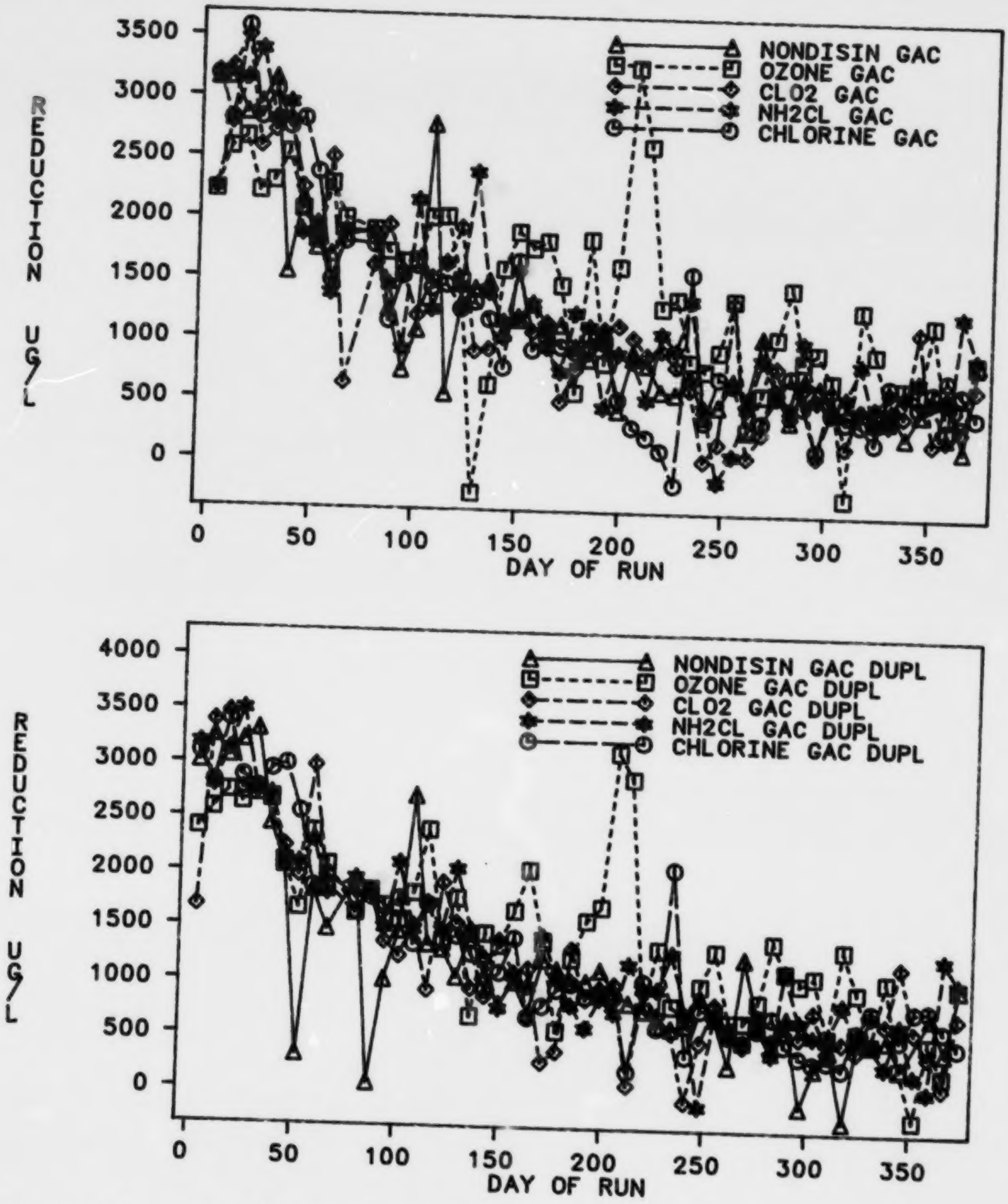


Figure 26. Comparison of the TOC Reductions Observed Across each GAC and GAC Duplicate Column.

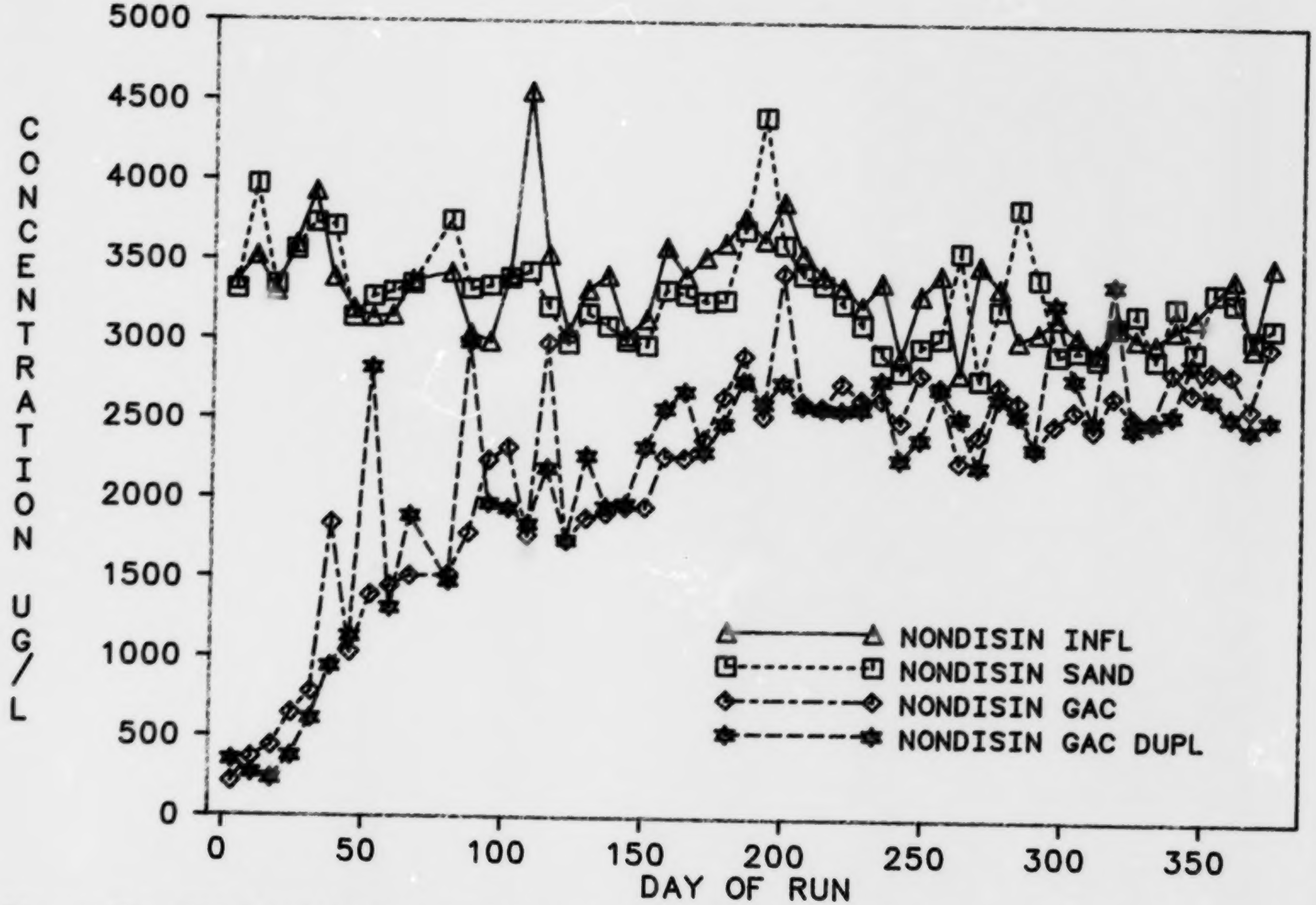


Figure 27. TOC Breakthrough Profiles for the Nondisinfected Process Stream.

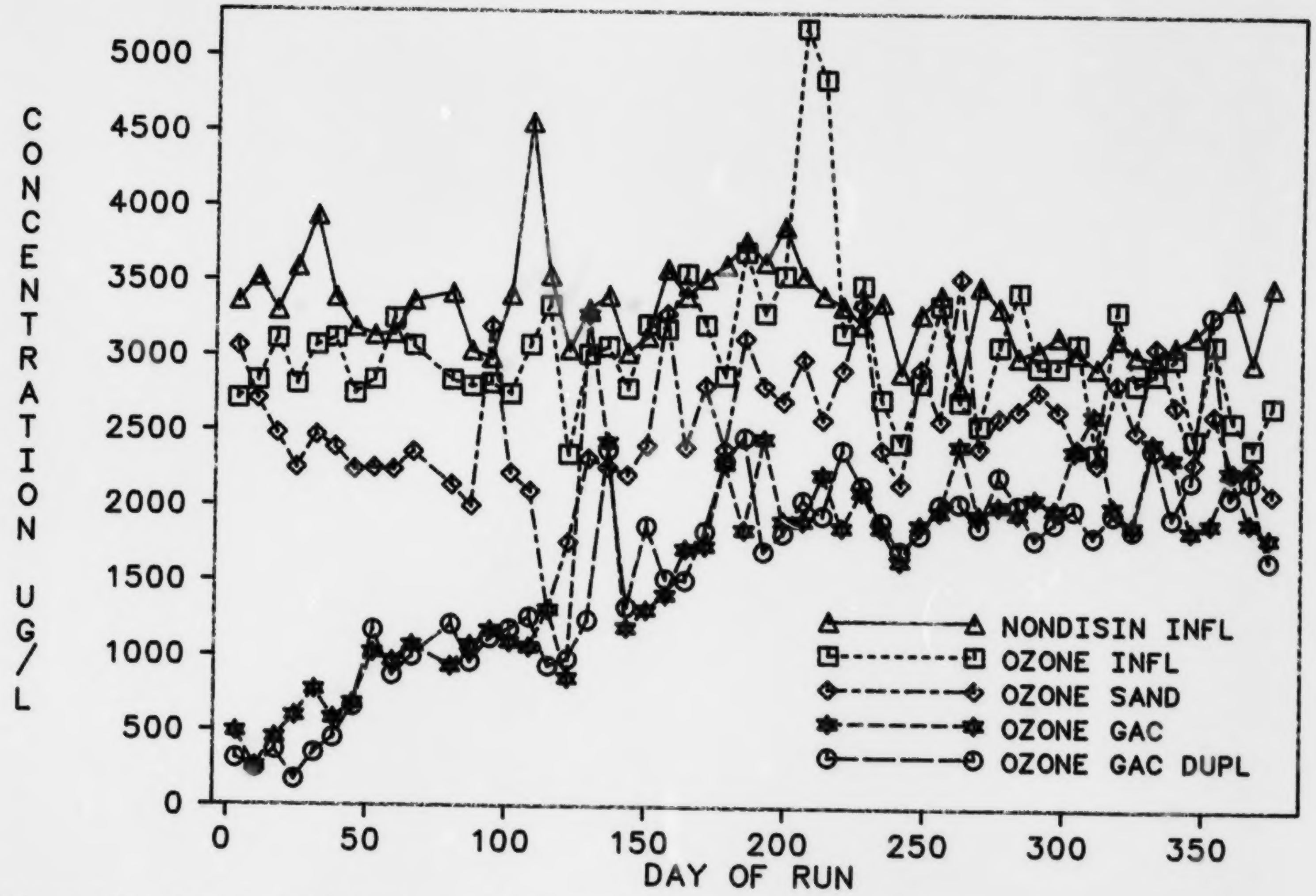


Figure 28. TOC Breakthrough Profiles for the Ozone Process Stream.

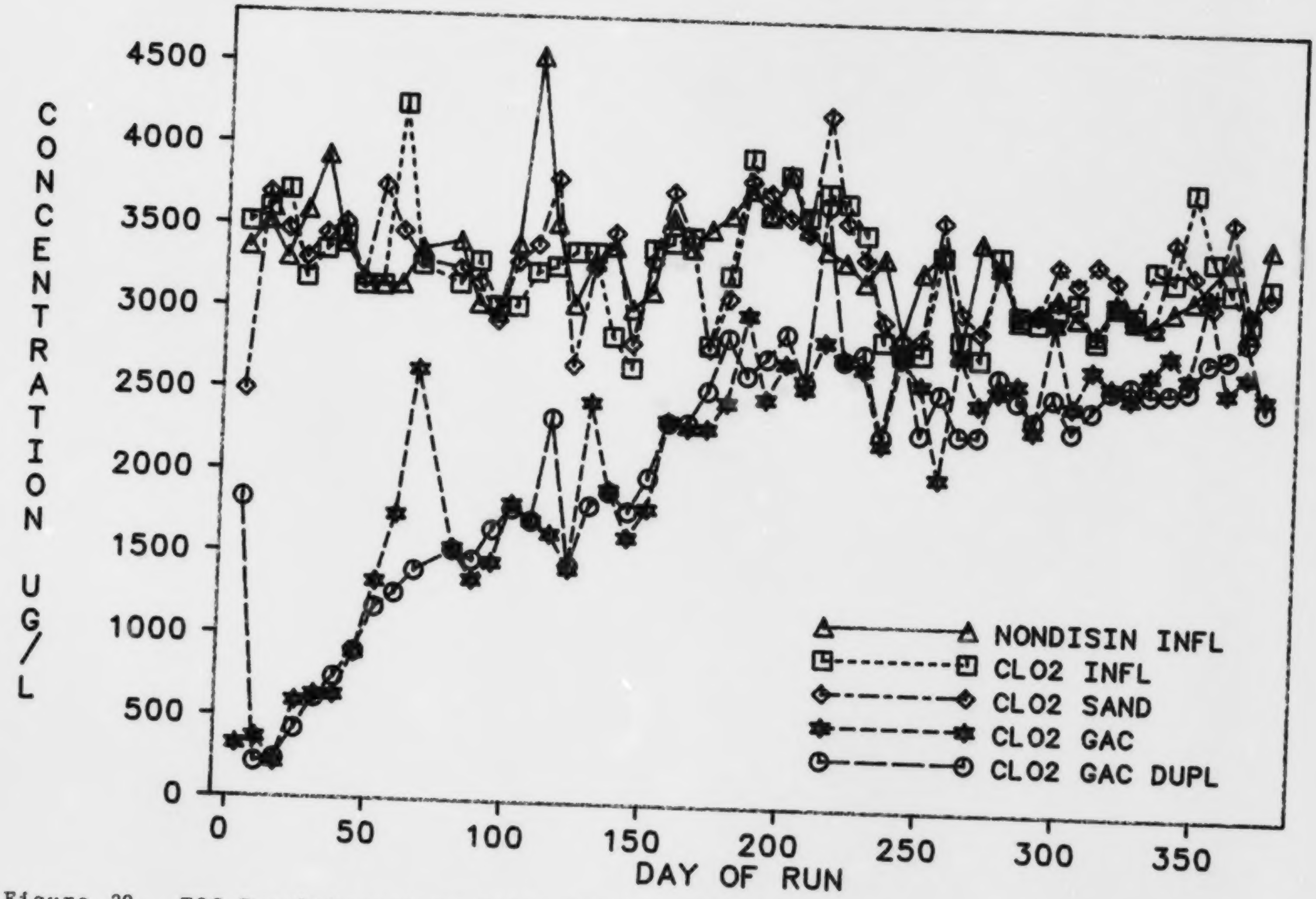


Figure 29. TOC Breakthrough Profiles for the Chlorine Dioxide Process Stream.

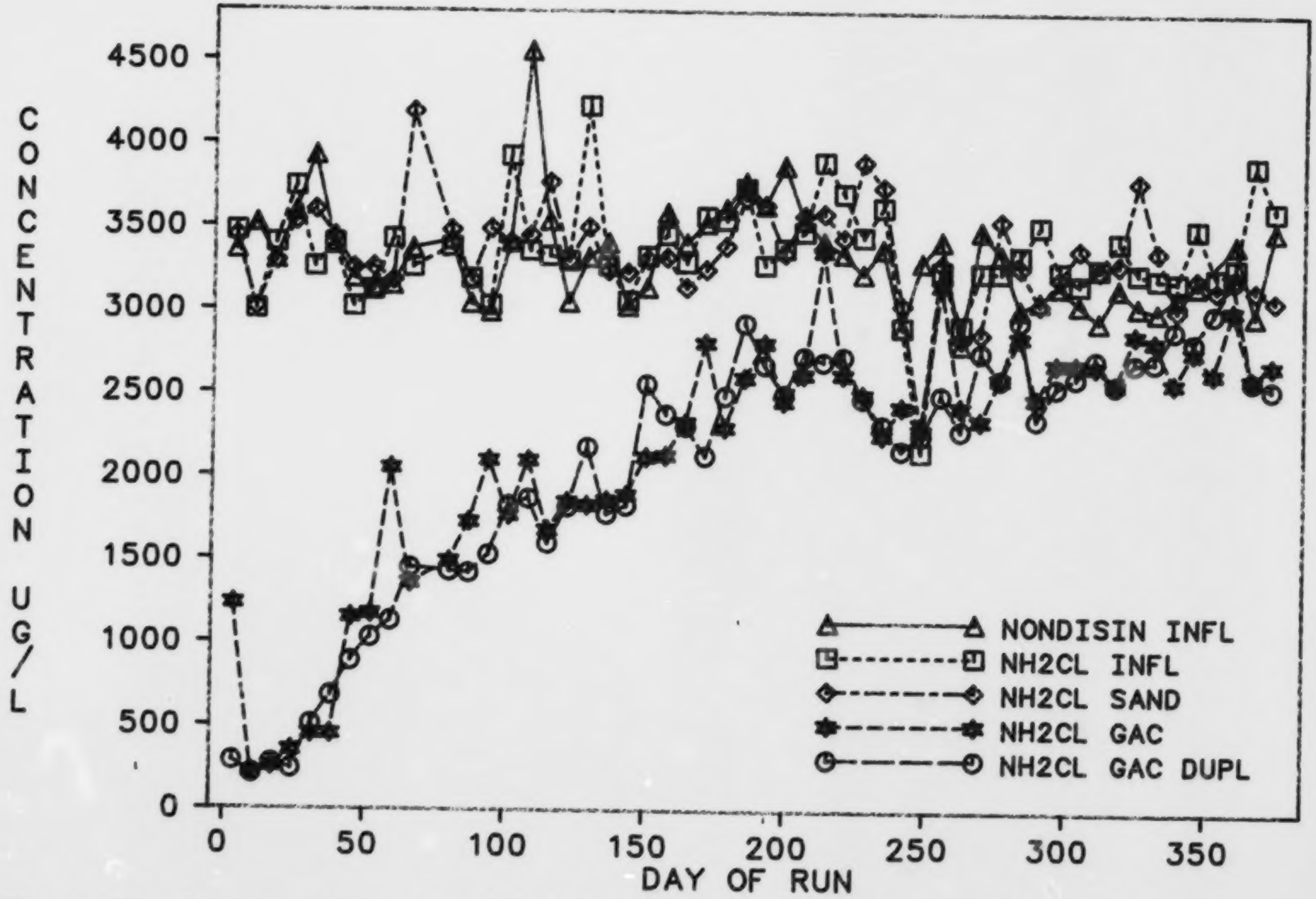


Figure 30. TOC Breakthrough Profiles for the Chloramine Process Stream.

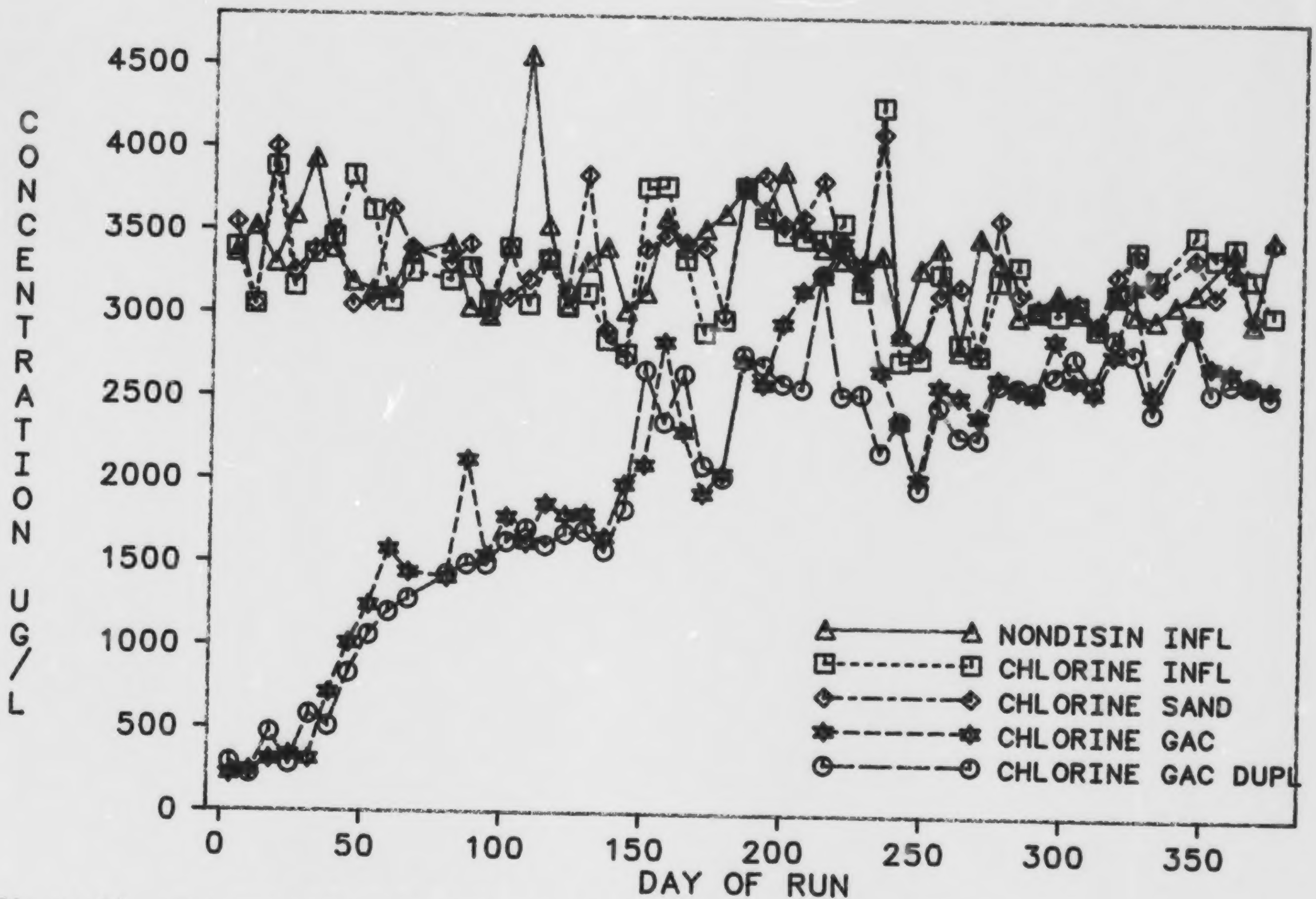


Figure 31. TOC Breakthrough Profiles for the Chlorine Process Stream.

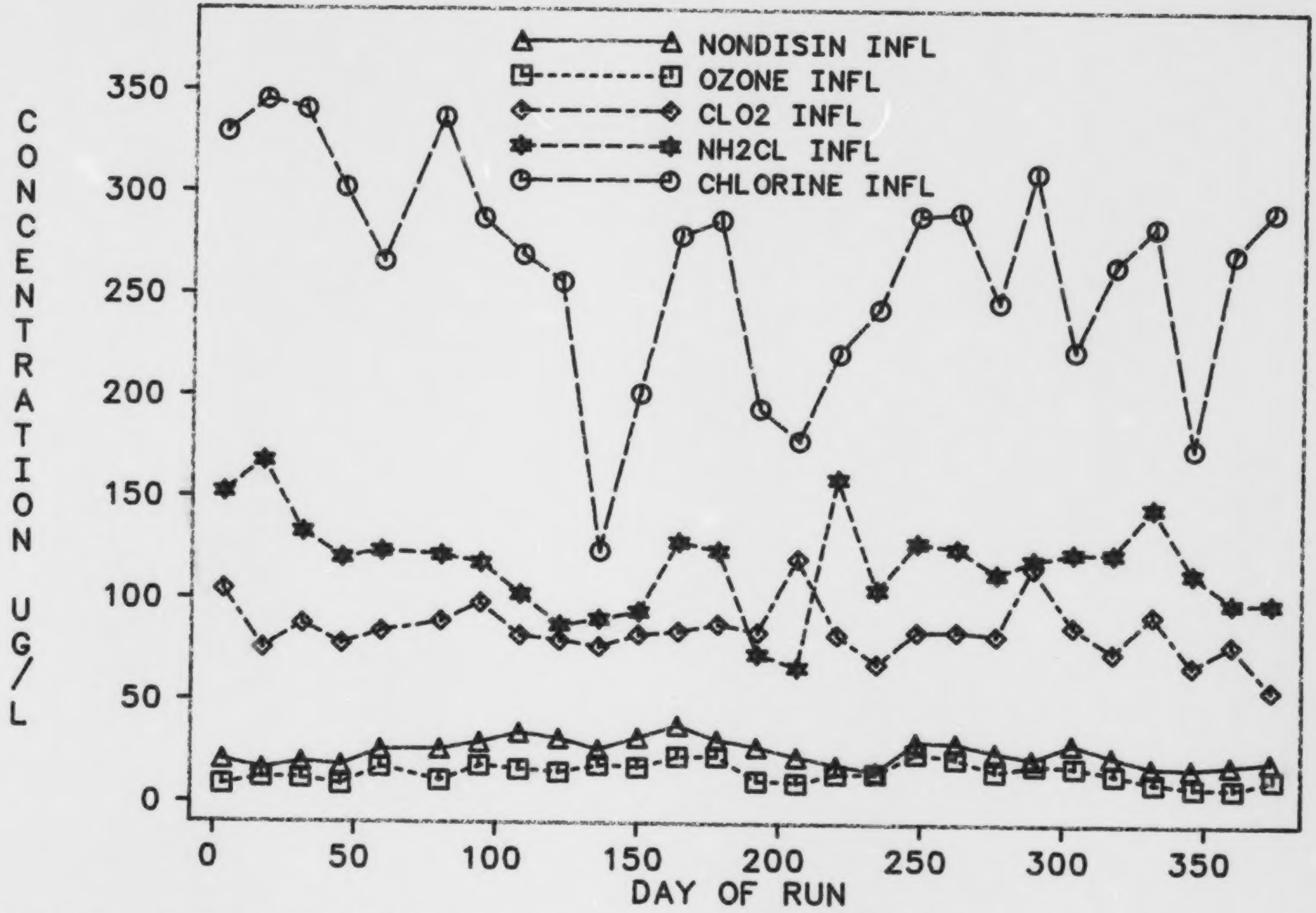


Figure 32. Comparison of the TOX Influent Levels for each Process Stream.

minutes of disinfectant contact time were 50, 92, and 238 ug/l, respectively, while contact with ozone for 30 minutes resulted in an average reduction of 10 ug/l TOX.

Toward the end of the operational period, it was realized that the ammonium hydroxide pump operated on a pulsed cycle such that ammonium hydroxide was intermittantly injected into the chloramine stream ahead of the chlorine eductor with a pulse interval of approximately 9 seconds. Thus, approximately one half of the influent water in the chloramine stream came into contact with free chlorine for a very short period of time estimated at approximately 4 seconds before entrance into the chloramine contact chamber at which point excess ammonia in the chamber would immediately react with any free chlorine present to produce chloramine. To evaluate the effect of this brief contact with free chlorine, the chlorine dioxide stream was converted to a second chloramine stream after the operational period had ended. This second chloramine system differed from the first in that both ammonium hydroxide and sodium hypochlorite were premixed prior to introduction into the chloramine process stream. The 30 minute chloramine residuals produced at a water temperature 10°C by the original system were 1.3 mg/l NH_2Cl and 0.3 mg/l $NHCl_2$ while those produced by the premixed system were 1.4 mg/l NH_2Cl and 0.0 mg/l $NHCl_2$. There was no free chlorine residual observed in either system at this time. The results of this evaluation, which was performed in duplicate, showed that with an influent TOX level of 29 ug/l, 30 minutes of disinfectant contact time in the original chloramine stream produced a TOX level of 75 ug/l while the TOX level in the effluent of the disinfectant contact chamber of the premixed chloramine stream was only 33 ug/l. These data imply that essentially all of the TOX formed in the original chloramine stream was formed during the brief contact with free chlorine which resulted from the ammonium hydroxide being pulsed into the chloramine stream. This underlies the importance of the logistics of chlorine and ammonia addition in the generation of chloramines. The effect of this brief contact with free chlorine was also examined with respect to the formation of trihalomethanes (THMs), the results of which will be discussed in a subsequent section. However, it should be noted that while 46 ug/l of TOX was formed during the brief contact with free chlorine, only 3 ug/l of this total was attributable to the formation of THMs. This indicates that Mississippi River water also contains other TOX precursors that are much more reactive than those which produce THMs as has been indicated for other drinking water sources.

Another post operational period evaluation was conducted on the ozone stream in order to determine if the observed TOX reduction was the result of gas purging of volatile TOX or the result of actual oxidation of TOX by ozone. For this evaluation, the ozonation equipment was operated in the normal manner with the ozone generator "on" producing a 30 minute ozone residual of 0.54 mg/l, and also with the ozone generator "off" such that only compressed air passed through the ozone contact chamber. The results of this evaluation which was performed in duplicate showed that with an influent TOX level of 29 ug/l, air purging without ozone reduced the level of TOX to 22 ug/l while air purging with ozone reduced the level to 17 ug/l. This indicates that a large portion of the TOX reduction across the ozone contact chamber was attributable to air purging (at 5 SCFH) with the remainder being attributable to oxidation by ozone. As will be indicated in the subsequent sections, no detectable reduction of trihalomethanes or 1,2-dichloroethane was observed across the ozone contact chamber indicating that this decrease in TOX resulted from the presence of some other as yet unidentified halogenated volatile organic substances. After a period of four months had elapsed, all of the aforementioned post operational period evaluations were again repeated at a water temperature of 29°C with similiar results.

The levels of TOX observed in the effluent of the sand column of each process stream are compared in Figure 33. These levels are essentially the same as those of their respective influents with average TOX levels of 23, 14, 83, 117, and 258 ug/l for the nondisinfected, ozone, chlorine dioxide, chloramine and chlorine sand columns, respectively. Thus, the increased biological activity observed for ozone sand column had only a marginal effect on the removal of TOX.

As might be expected, the levels of TOX in the effluent of the GAC and GAC duplicate columns exhibited similiar trends as that of their influents as indicated in Figure 34. That is to say, the higher the influent level of TOX, the faster the breakthrough and the higher the effluent level of TOX. Also, as can be seen in Figure 35 which compares the reductions of TOX across each GAC column, the greater the influent concentration of TOX, the greater the GAC loading of TOX. These data indicate that while a higher influent concentration resulted in a higher level of GAC loading, it is the lowest influent concentration which produced the lowest effluent concentration. Thus, the optimim GAC system relative to TOX removal would be one that minimized influent TOX levels, i.e. nondisinfected and ozone systems or possibly a properly generated chloramine system.

The breakthrough profiles of TOX through the GAC and GAC duplicate columns of each process stream are presented in Figures 36-40. The nondisinfected GAC columns reached a "steady state" condition on or about day 220 with an effluent TOX level of 18 ug/l while that for the ozone GAC columns occurred on day 190 at the 13 ug/l level. The concentration differential between influent and effluent TOX levels after "steady state" had been reached was approximately 5 ug/l for both the non-disinfected and

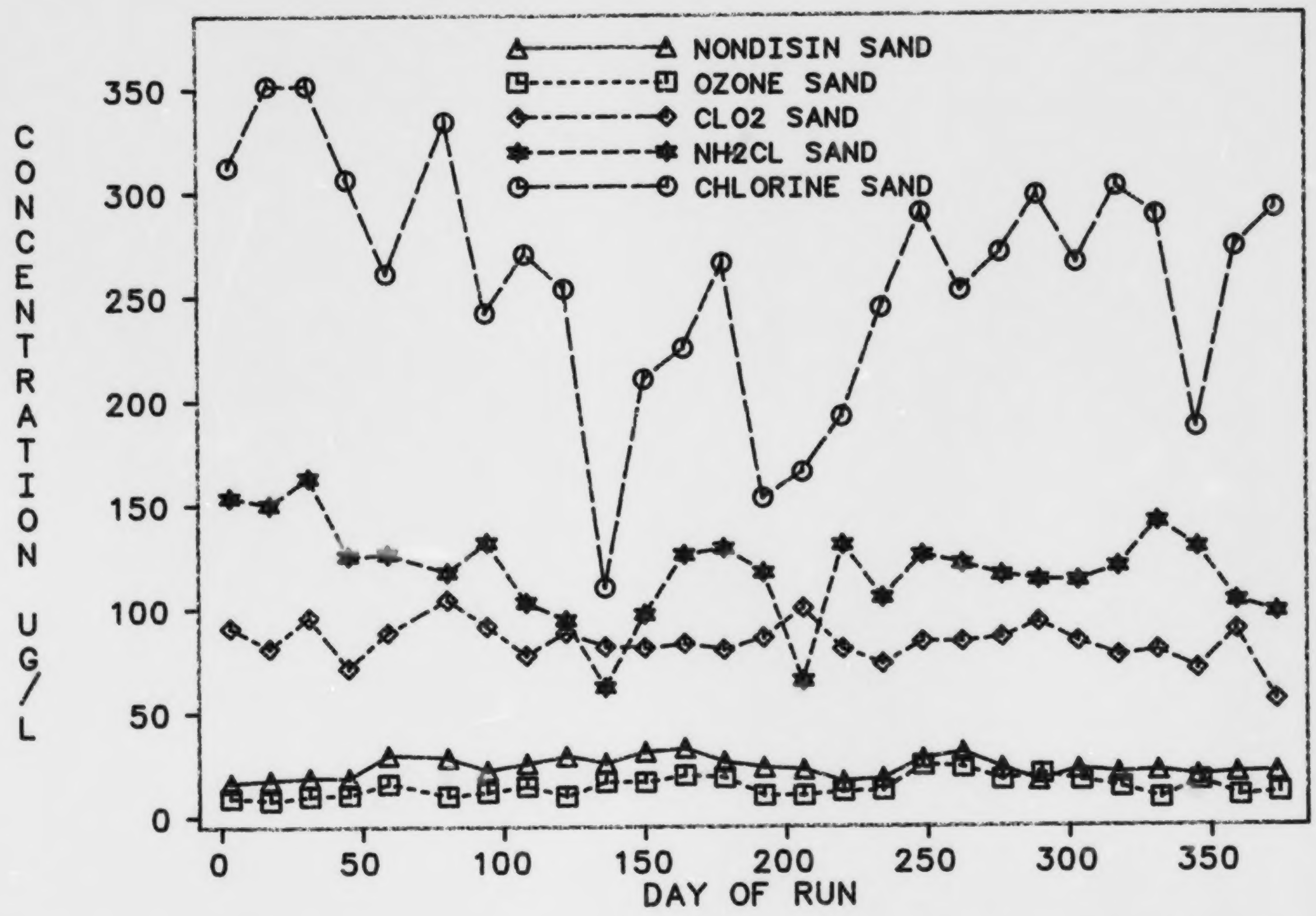


Figure 33. Comparison of the TOX Sand Effluent Levels for each Process Stream.

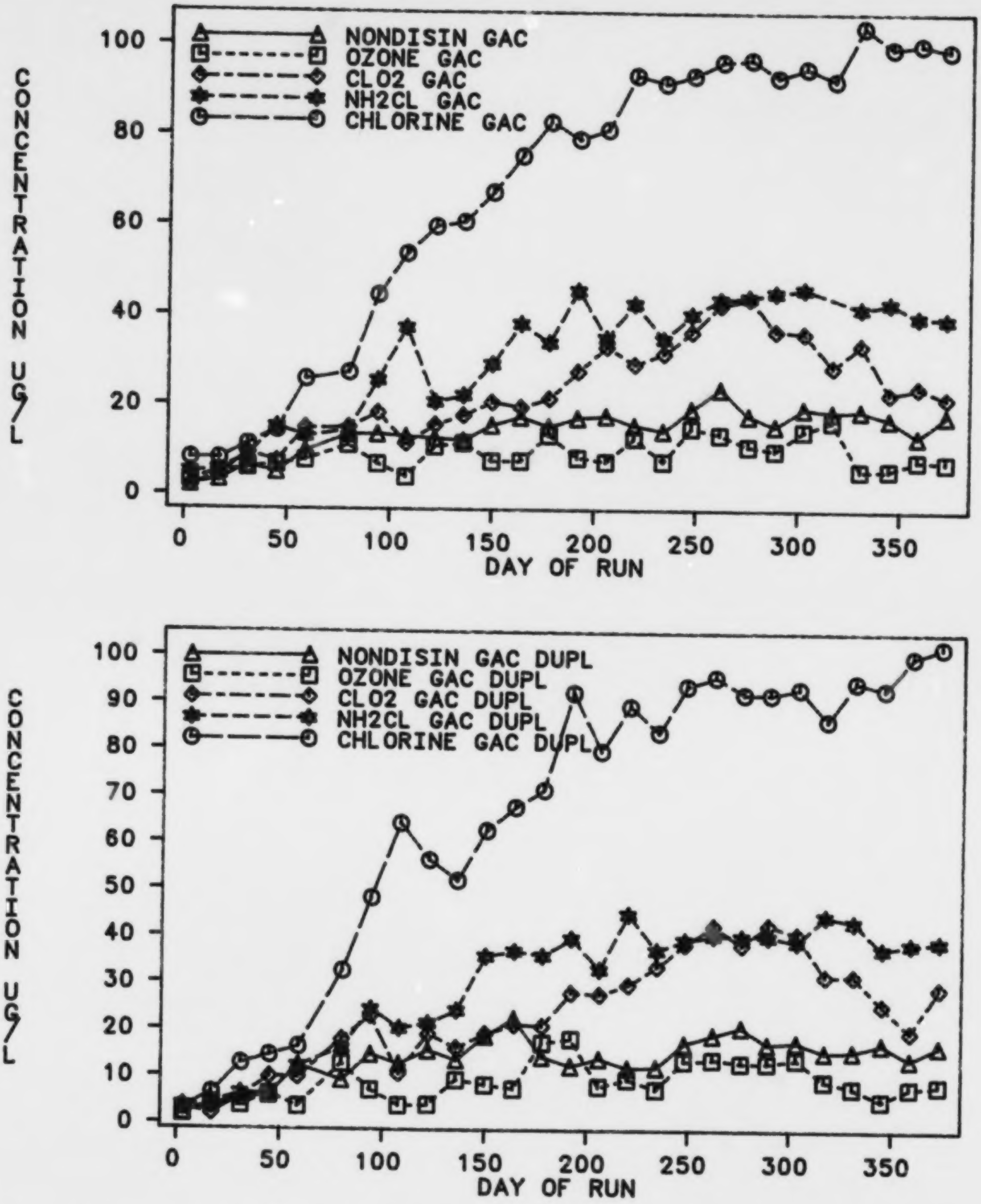
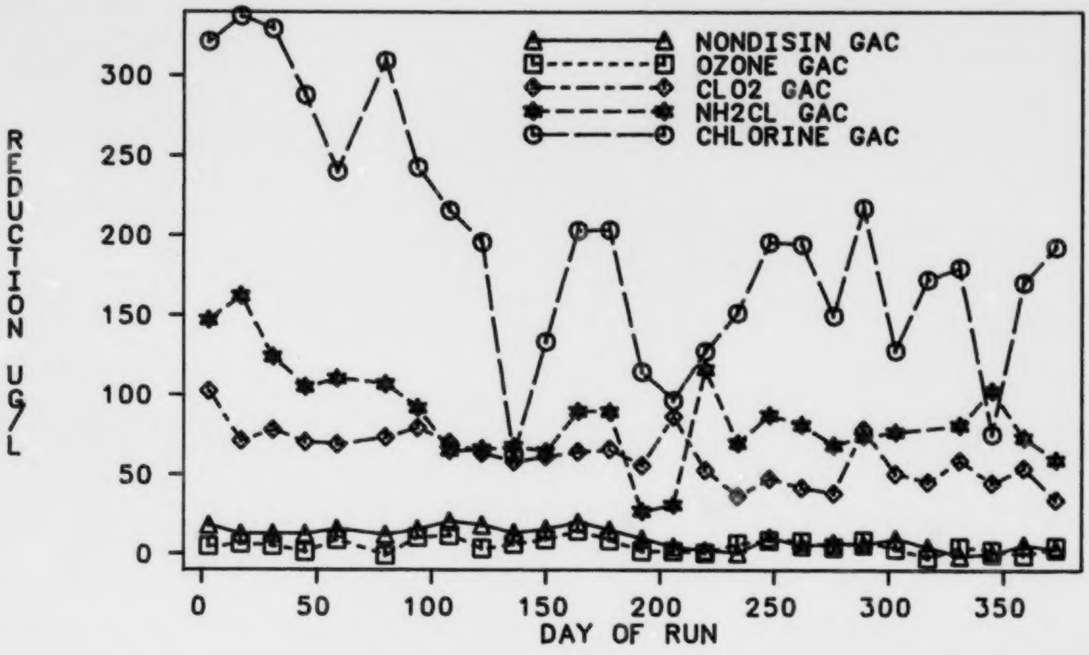


Figure 34. Comparison of the TOX GAC and GAC Duplicate Effluent Levels for each Process Stream.



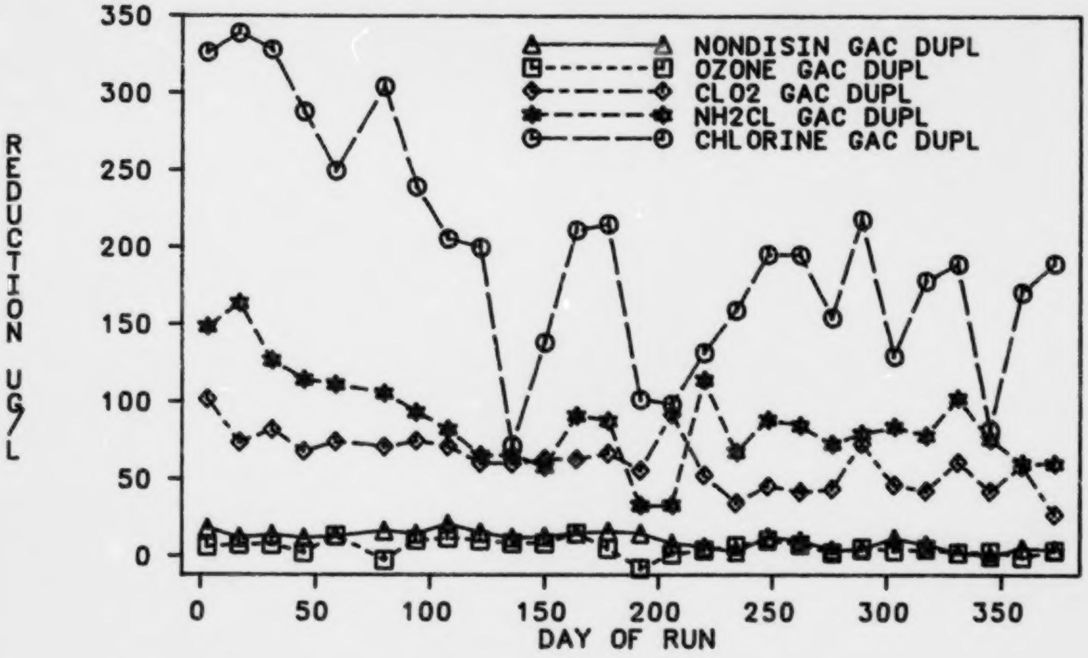


Figure 35. Comparison of the TOX Reductions Observed Across Each GAC and GAC Duplicate Column.

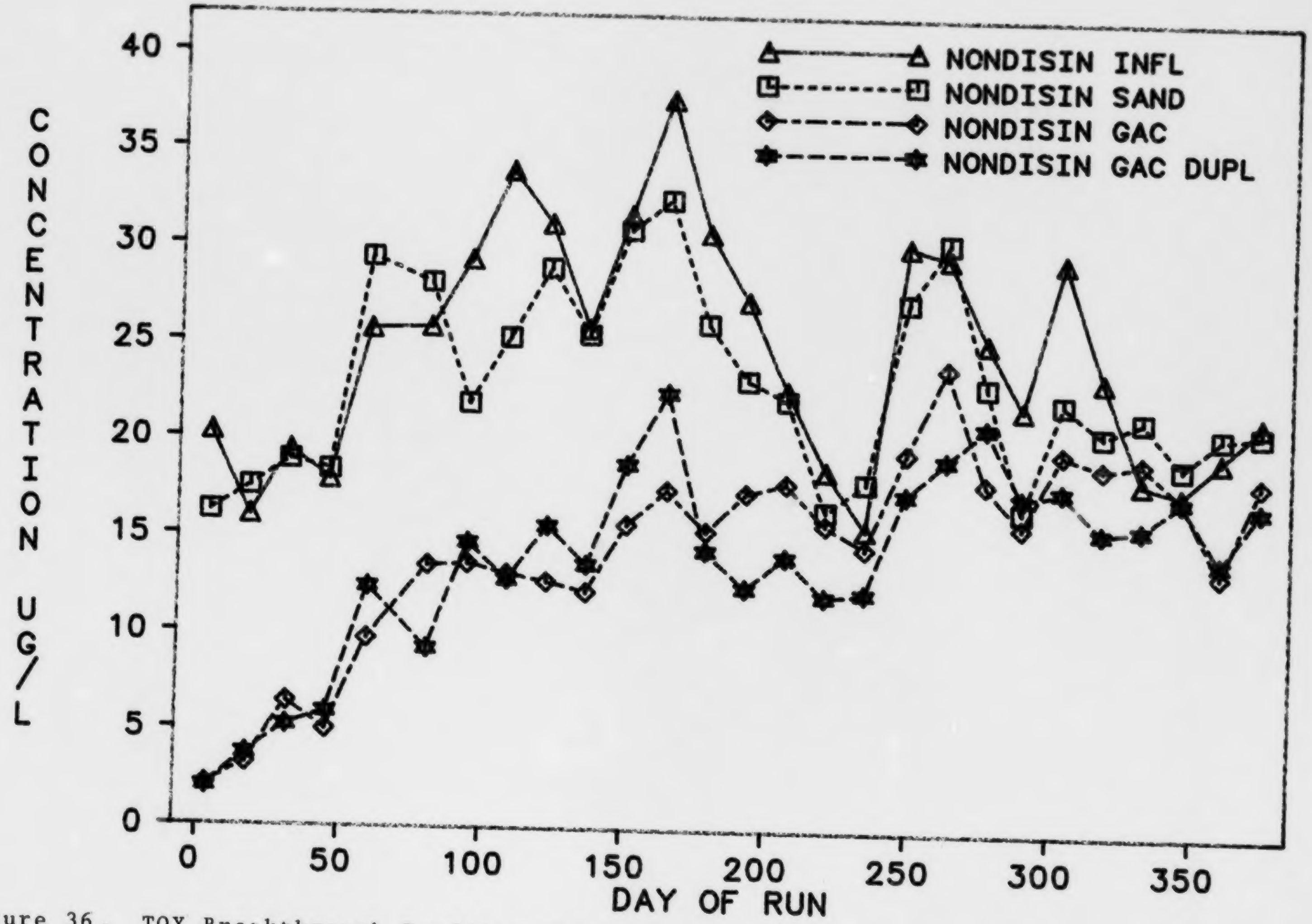


Figure 36. TOX Breakthrough Profiles for the Nondisinfected Process Stream.

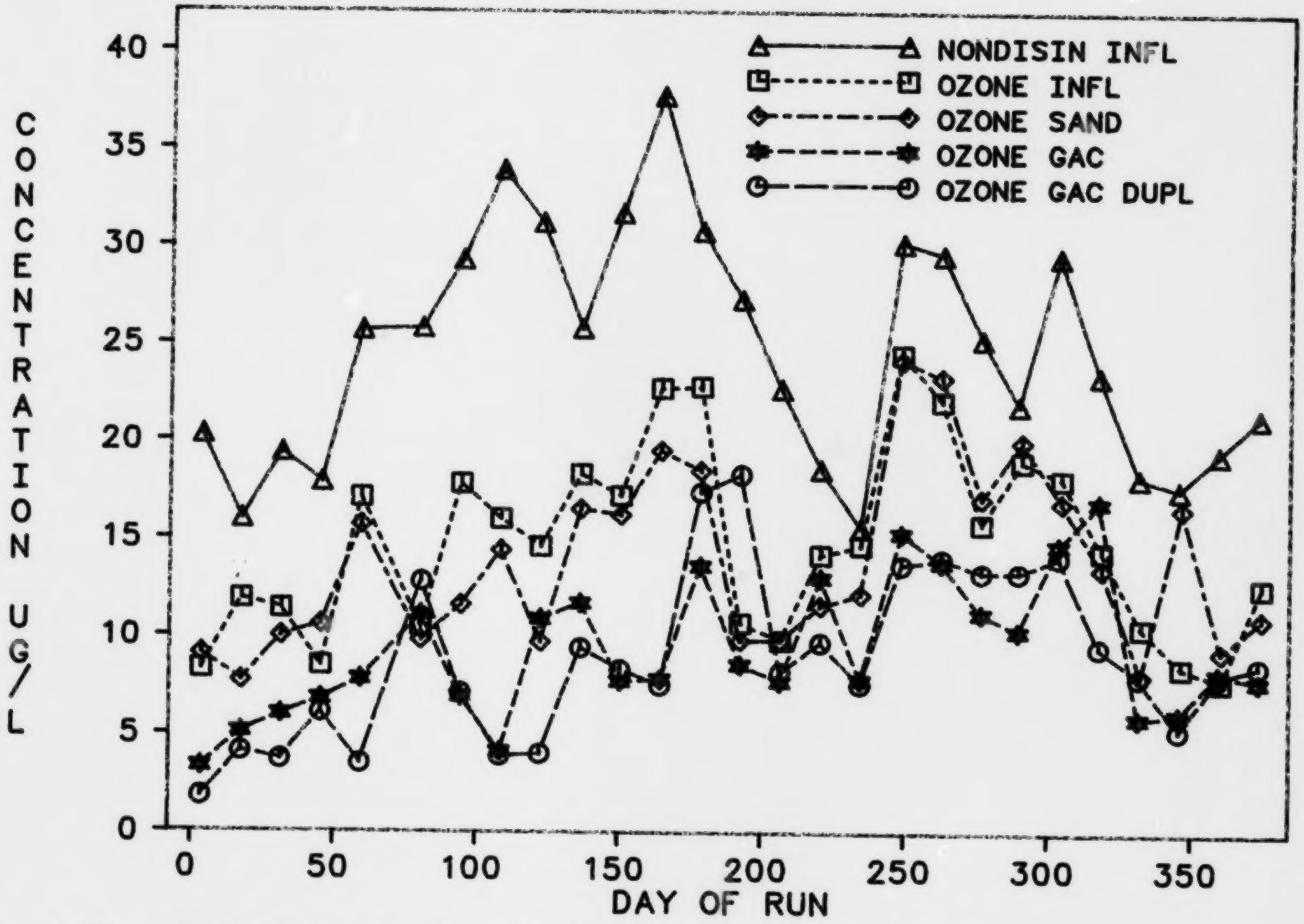


Figure 37. TOX Breakthrough Profiles for the Ozone Process Stream.

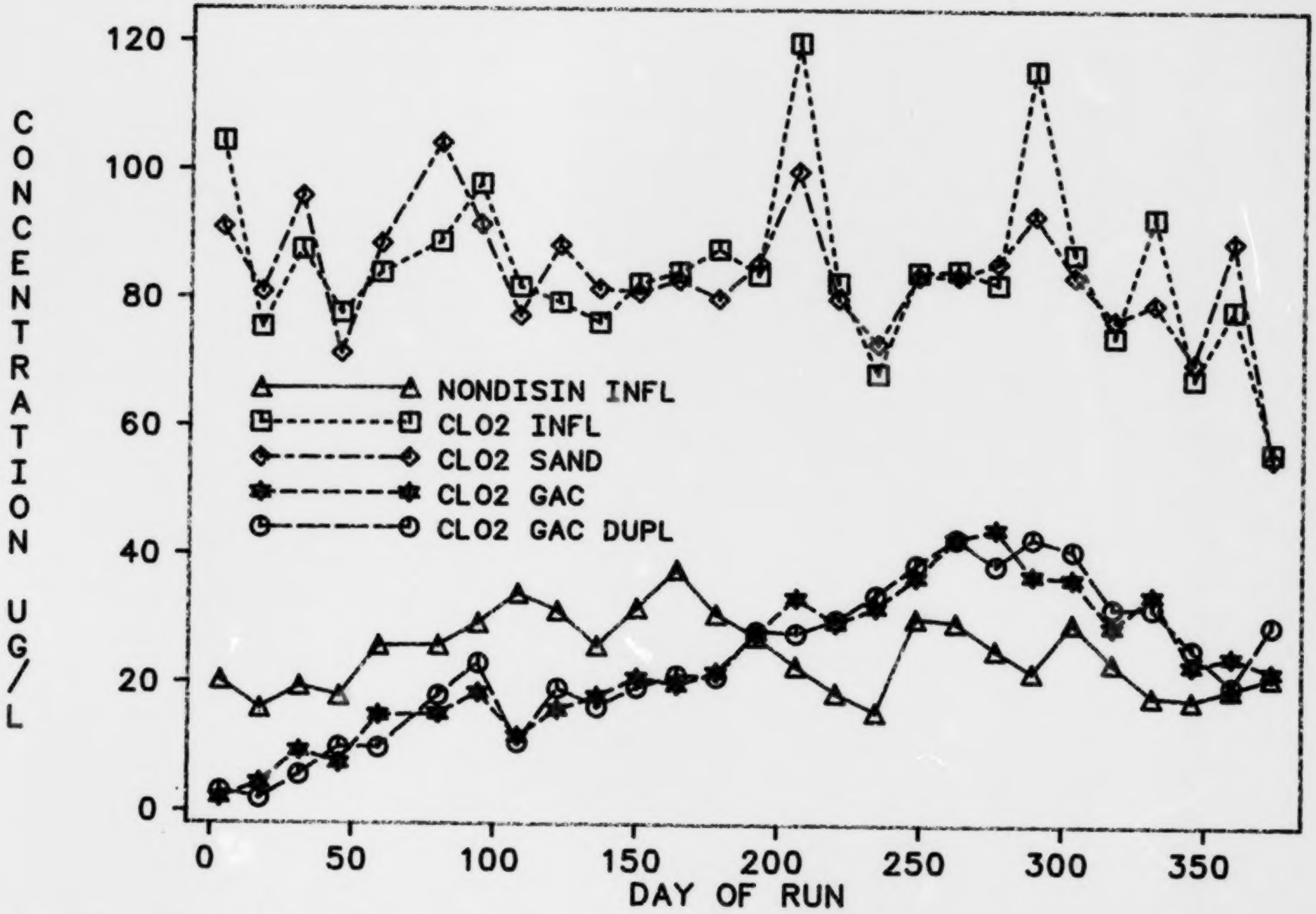


Figure 38. TOX Breakthrough Profiles for the Chlorine Dioxide Process Stream.

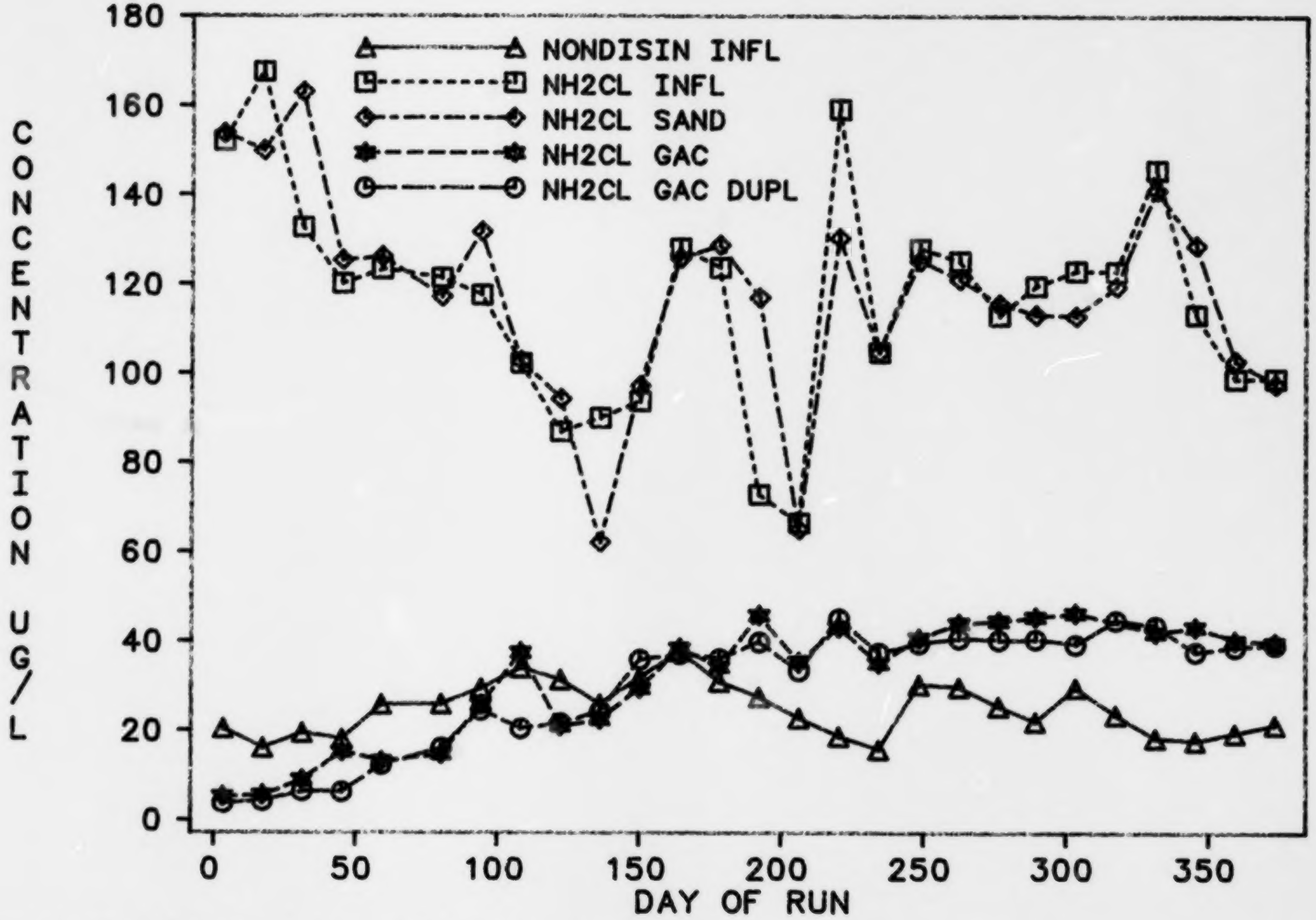


Figure 39. TOX Breakthrough Profiles for the Chloramine Process Stream.

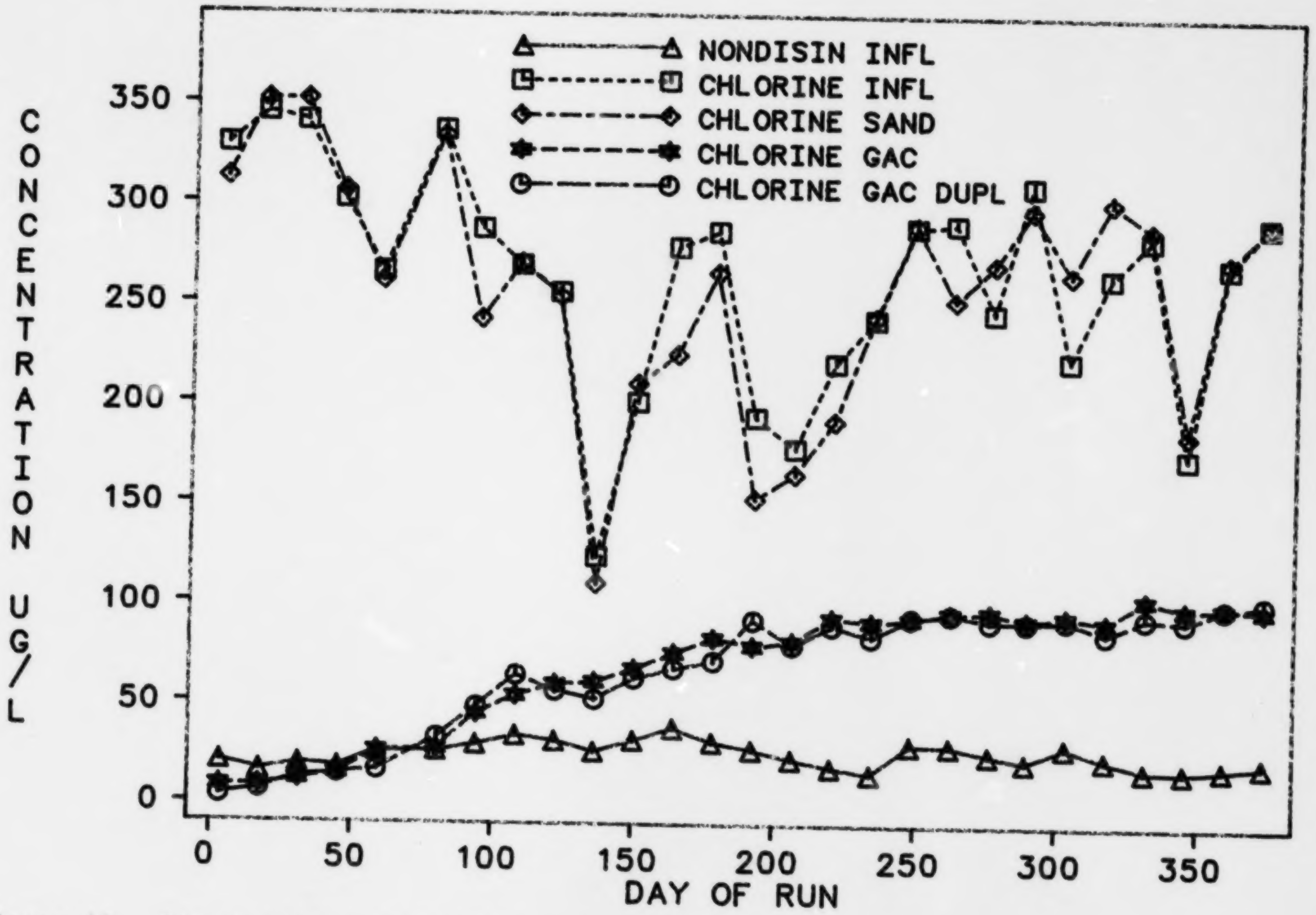


Figure 40. TOX Breakthrough Profiles for the Chlorine Process Stream.

ozone GAC columns. While the chlorine dioxide and the chloramine GAC columns all reached the "steady state" condition at approximately the same concentration of 40 mg/l, the duration to "steady state" was 40 days longer for the chlorine dioxide columns at 260 days than for the chloramine columns at 220 days. Also, the concentration differential at "steady state" between influent and effluent TOX levels was twice as great for the chloramine GAC columns at 80 ug/l than for the chlorine dioxide GAC columns at 40 ug/l. While the chlorine GAC columns also reached "steady state" on day 220, the TOX "steady state" effluent concentration was 90 ug/l with a concentration differential of 175 ug/l between influent and effluent TOX levels at "steady state". These data further illustrate the effect of higher GAC loading associated with a higher influent concentration and indicate that influent concentration does not appear to be a major factor in ascertaining GAC bed life.

TERMINAL TOX --

In general, the terminal TOX levels observed in those samples treated with free chlorine (TOX-Cl_2) are indicative of total TOX potential while the terminal TOX levels observed for those samples treated with chloramines (TOX-NH_2Cl) display the relatively low reactivity of chloramines with TOX precursors. A comparison of the average terminal TOX-CL_2 levels observed for each sample location are presented in Figure 41 along with each location's respective average instantaneous TOX level. Average TOX precursor reductions of approximately 184 ug/l (35%) and 151 ug/l (29%) were observed after 30 minutes of contact with ozone (O_3) and chlorine dioxide (ClO_2), respectively. On the average, after 30 minutes of contact with chlorine dioxide, approximately 17% of the total available TOX precursors were converted to TOX. Some portion of this TOX undoubtly resulted from the reaction of TOX precursor with an estimated 0.1-0.2 mg/l of unreacted hypochlorite remaining from the generation of chlorine dioxide. During the same contact period with free chlorine (Cl_2), 49% of the total available TOX precursors were converted to TOX.

In general, similiar results were observed for the effluents of the sand column of each system except for slight TOX precursor reductions of 31 ug/l and 62 ug/l for the ozone (O_3) and the nondisinfected (ND) sand columns, respectively. While the biological activity in the effluents of these columns suggests that the greater biodegredation of TOX precursors should have occurred on the ozone sand column, it is logical to assume that a large portion of the biodegradable TOX precursors were reduced in the ozone contact chamber. These data also indicate that the ozonation of TOX precursors does not significantly increase the biodegradability of these substances.

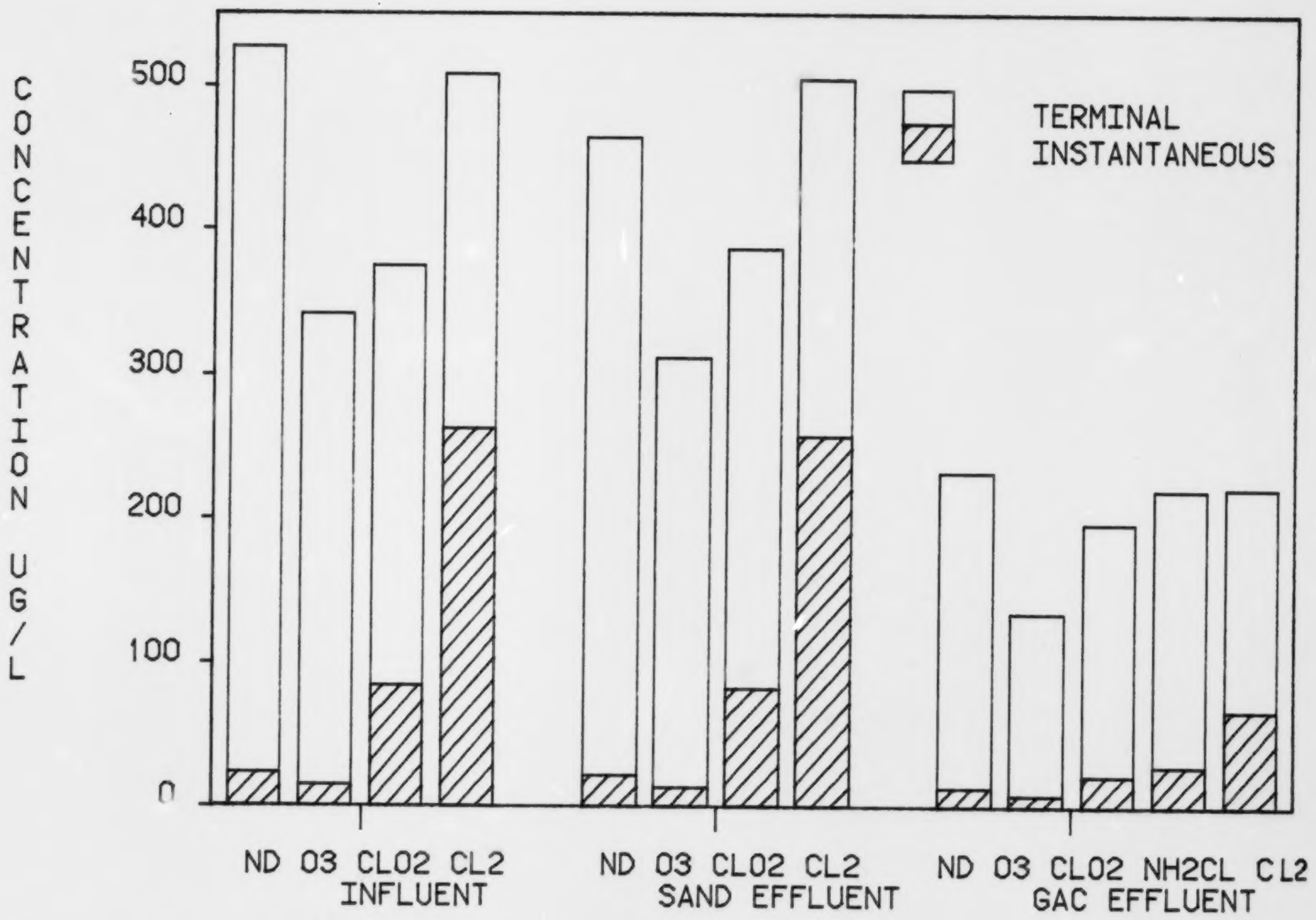


Figure 41. Average Terminal TOX-CL_2 Levels After the Addition of Free Chlorine and Storage for 5 Days at 28oC.

Similiar average terminal TOX-Cl_2 levels ranging from 220-230 ug/l were observed after GAC filtration for the nondisinfected, chloramine, and chlorine systems. The average effluent concentration of the chlorine dioxide GAC columns was somewhat lower at 198 ug/l while that for the ozone GAC columns was considerabley lower at 135 ug/l. A comparison of the terminal TOX-CL_2 breakthrough profiles of each disinfectant system is presented in Figure 42. In this figure it is apparent that approximately 20 ug/l of TOX precursor material was unaffected by contact with any of the disinfectants and by GAC filtration as indicated by the initial horizontal section of each breakthrough profile.

A comparison of the average terminal TOX-NH_2Cl levels observed for each sampling location are presented in Figure 43 along with each location's respective average instantaneous TOX level. These average TOX levels are only partially indicative of TOX precursor removal. The primary effect observed is that of the nonreactivity of chloramines. The average terminal TOX-NH_2Cl levels for the nondisinfected and ozone influents and sand column effluents were essentially twice that of their respective instantaneous TOX levels. However, the average TOX-NH_2Cl for the ozone sand column effluent was 35% lower than that for the ozone influent which can be attributed to the microbiological degradation of TOX precursors.

Comparison of the average TOX-I and TOX-NH_2Cl levels for the influents and sand column effluents of the chlorine dioxide and chloramine systems indicate that a significant reduction in TOX-I occurred upon the addition of chloramines for all locations whose average TOX-I levels was greater than 60 ug/l TOX. The average reductions for the influent and sand effluent of the chlorine dioxide system were 21% and 16%, respectively, while those for the NH_2Cl system were somewhat greater at 38% and 36%. This phenomena was also observed for the GAC effluent of the chlorine system with an average reduction of 6%. Efforts to reproduce this apparent anomaly in subsequent years has been unsuccessful suggesting that the cause may have been due to a variation in the type of TOX precursors present during this period. Further investigation has indicated that the addition of excess ammonia may result in a reduction in TOX across the 5 day incubation period. Limited testing has demonstrated reductions ranging from 0-10 ug/l.

The lowest terminal TOX NH_2Cl levels averaging 18 ug/l were observed for the ozone GAC effluent as indicated in Figure 44 while the highest levels averaging 62 ug/l were observed for the chlorine GAC effluent. Approximately 10 ug/l of TOX precursor material was unaffected by both disinfection and GAC filtration as indicated by the initial horizontal section of each breakthrough profile.

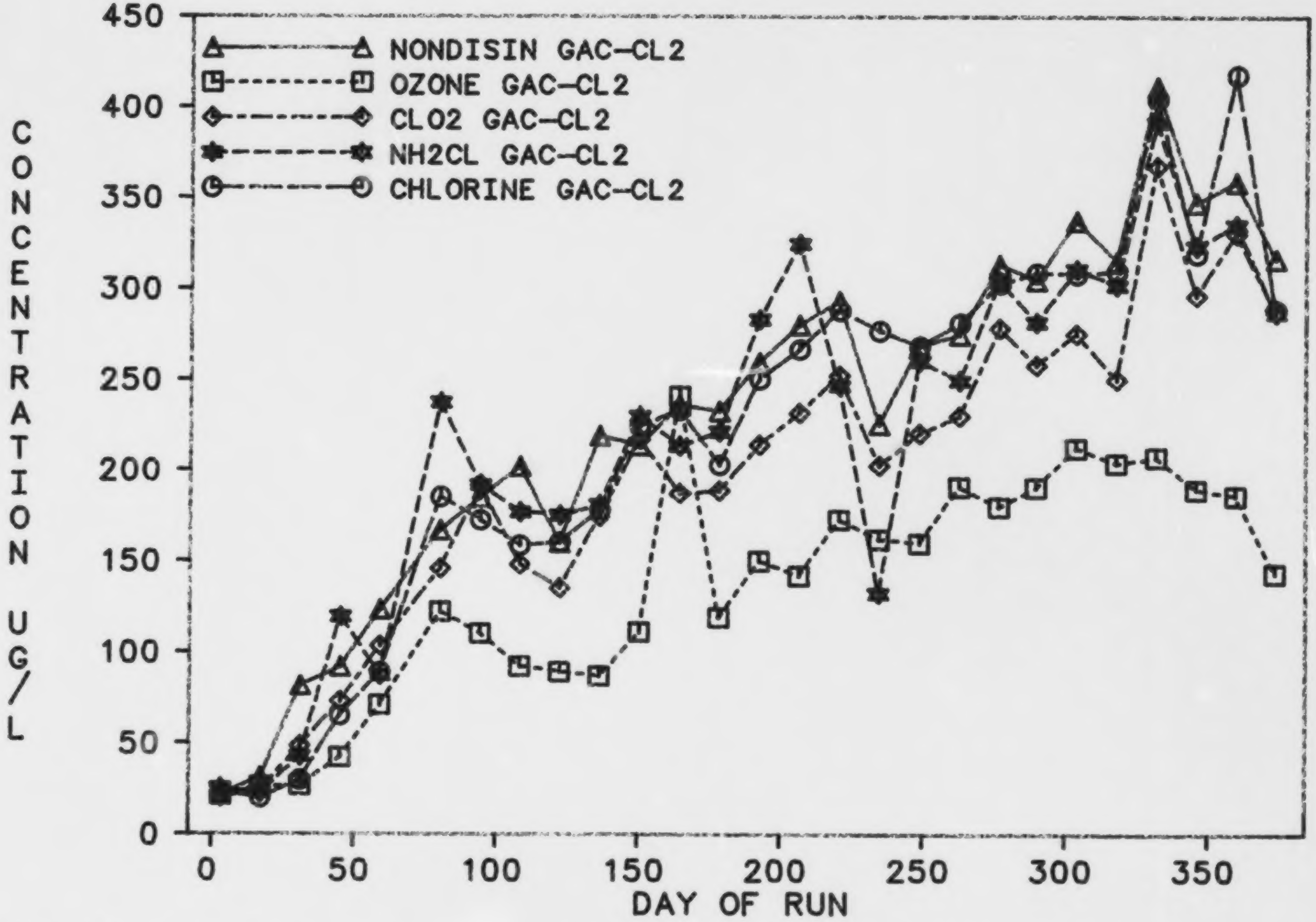


Figure 42. Comparison of the TOX-CL_2 GAC Effluent Levels for each Process Stream.

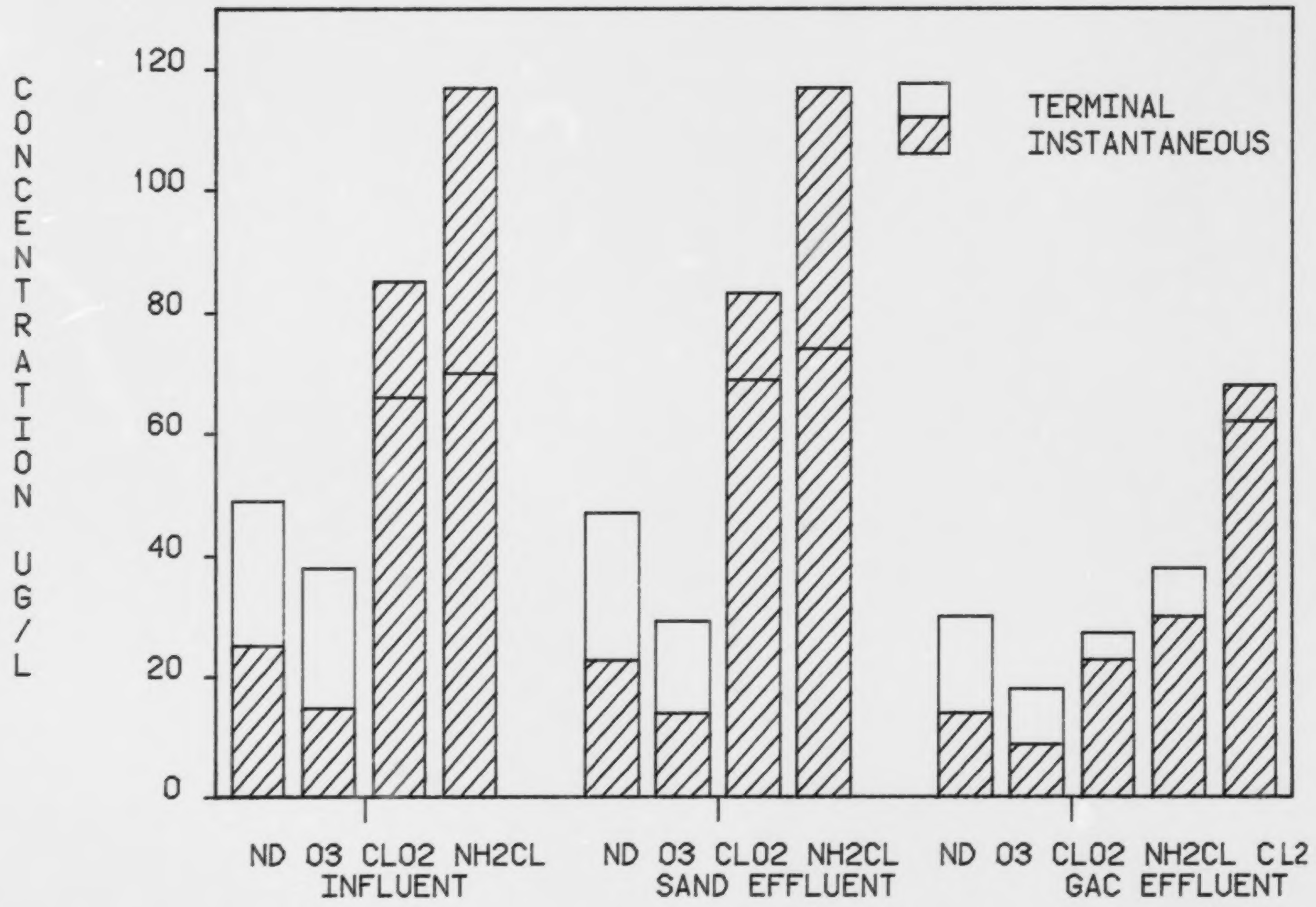


Figure 43. Average Terminal TOX-NH_2CL Levels After the Addition of Monochloramine and Storage for 5 Days at 28°C.

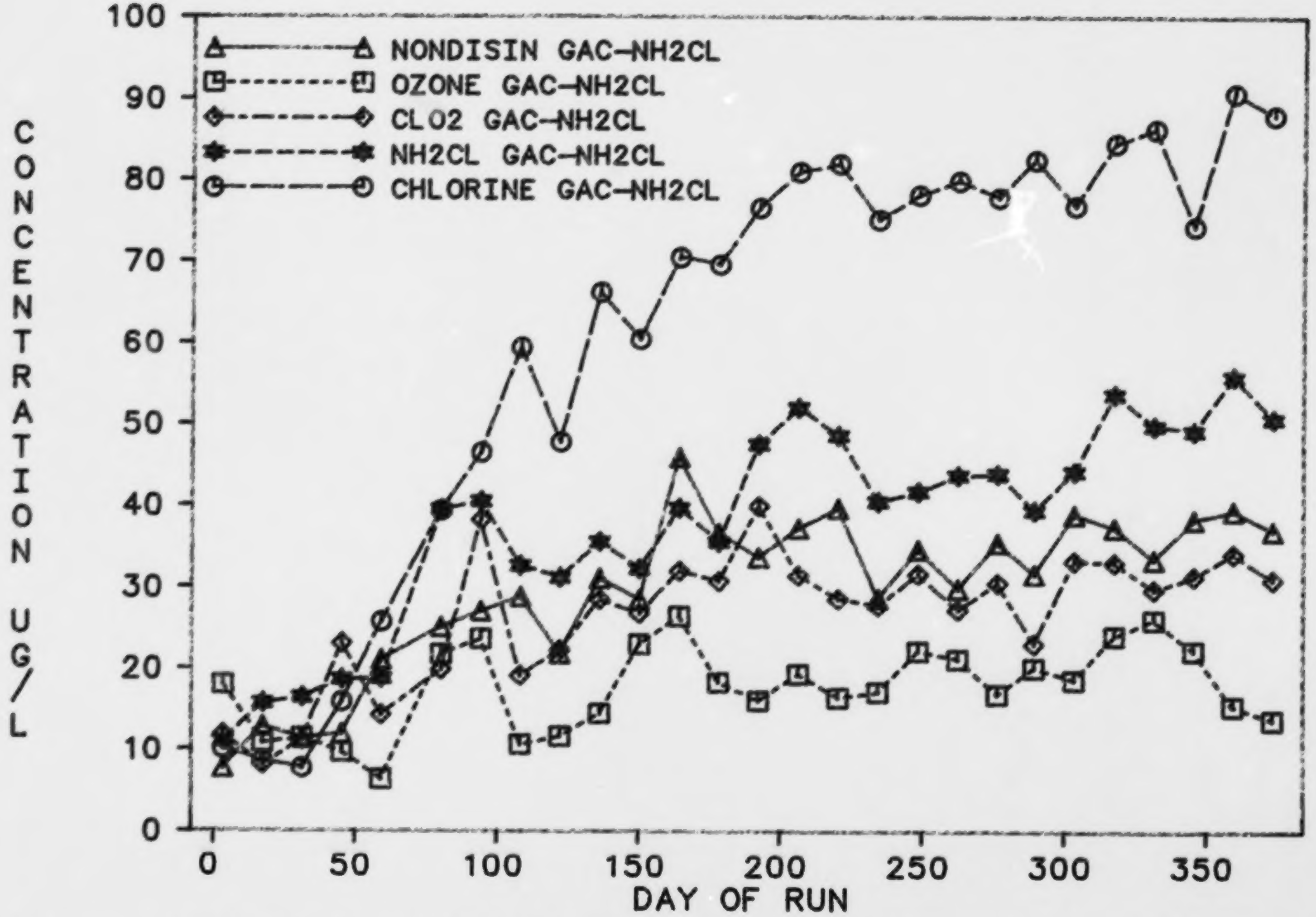


Figure 44. Comparison of the TOX-NH_2CL GAC Effluent Levels for each Process Stream.

The breakthrough profiles of terminal TOX-Cl_2 and TOX-NH_2Cl are presented for each process stream in Figures 45-48. The terminal TOX-Cl_2 levels in the combined effluents of the nondisinfected GAC columns reached a "steady state" condition around day 300 at the 350 ug/l level which was, on the average, 192 ug/l below that of its influent. In contrast, the terminal TOX-NH_2Cl levels in the combined effluents of these same columns reached a "steady state" condition on day 150 at the 35 ug/l level with an average reduction of 10 ug/l after day 150. The combined GAC effluents of the ozone system exhibited the lowest terminal TOX -Cl_2 and TOX-NH_2Cl levels. Terminal TOX-Cl_2 levels in the effluents of the ozone GAC columns reached "steady state" on day 300 at the 200 ug/l level with an average reduction of 147 ug/l after day 300 while, except for two outlying data points around day 100, "steady state" was reached for TOX-NH_2Cl on day 150 at the 20 ug/l level with an average reduction of 16 ug/l after day 150. The combined effluents of the chlorine dioxide system were the second lowest for TOX-Cl_2 and TOX-NH_2Cl with an average reduction of 70 ug/l observed after "steady state" on day 275 at the 300 ug/l level for TOX-Cl_2 and an average reduction of 38 ug/l observed at the 30 ug/l level after day 150 for TOX-NH_2Cl. Terminal TOX-Cl_2 levels of the combined GAC effluents of the chloramine and chlorine systems are compared in the upper portion of Figure 48. Both effluents reached "steady state" on day 275 at the 300 ug/l level thus indicating that there was no removal of TOX precursors through disinfection with chloramines. While the combined effluents of the chlorine system exhibited a 161 ug/l average reduction for TOX-Cl_2 at "steady state", that of the chloramine system showed an average increase of 251 ug/l over the terminal TOX-$NHCl_2$ levels of its influent. Terminal TOX-NH_2Cl levels for the combined effluents of the chloramine and chlorine systems are compared in the lower portion of this same figure. The combined GAC effluents of the chloramine system reached "steady state" on day 100 at the 40 ug/l level with an average reduction of 21 ug/l. The combined GAC effluents of the chlorine system reached "steady state" on day 200 at the 80 ug/l level. While comparison of this level to that of its influent indicates an average reduction of 407 ug/l, comparison to that of the chloramine influent shows an increase averaging 13 ug/l.

TRIHALOMETHANES (THMs)

INSTANTANEOUS THMs--

The trihalomethane species formed during the various disinfection processes which employed chlorine in some form, and their relative abundances were chloroform ($CHCl_3$) >> bromodichloromethane ($CHBrCl_2$) > dibromochloromethane ($CHBr_2Cl$) >> bromoform ($CHBr_3$) with $CHCl_3$ accounting for approximately 75% of the THMs present with very little $CHBr_2Cl$ and relatively no

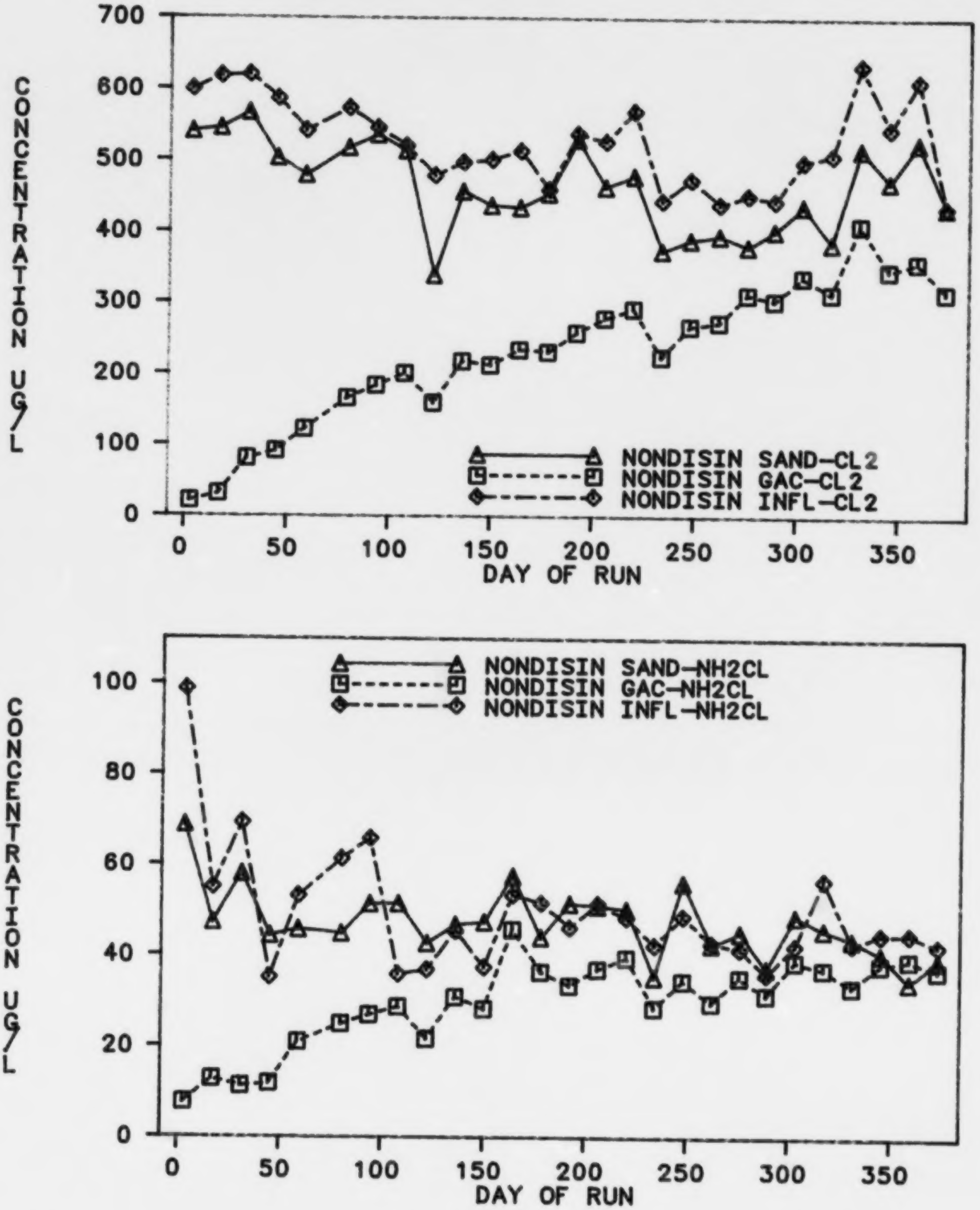


Figure 45. TOX-CL_2 and TOX-NH_2CL Breakthrough Profiles for the Nondisinfected Process Stream.

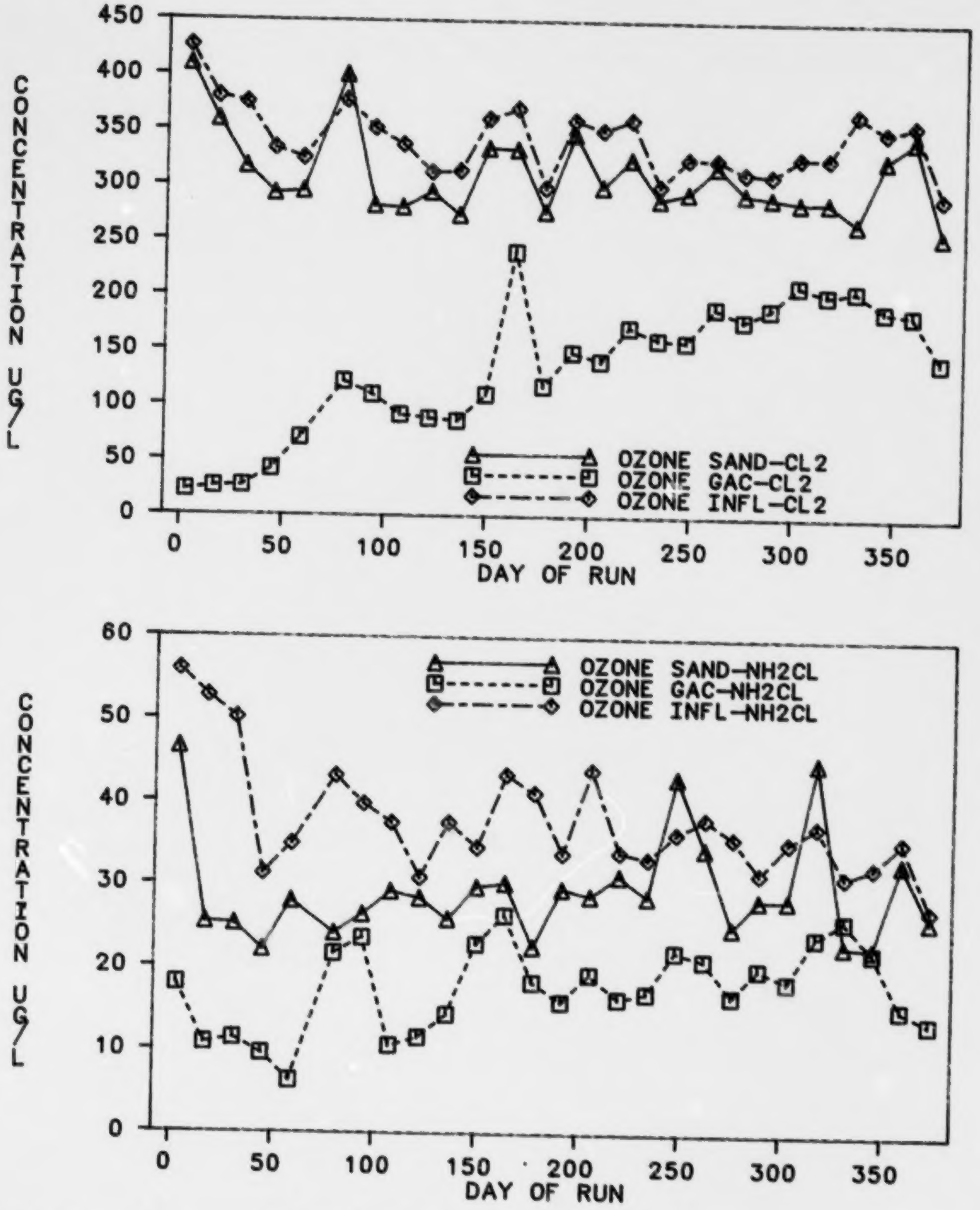
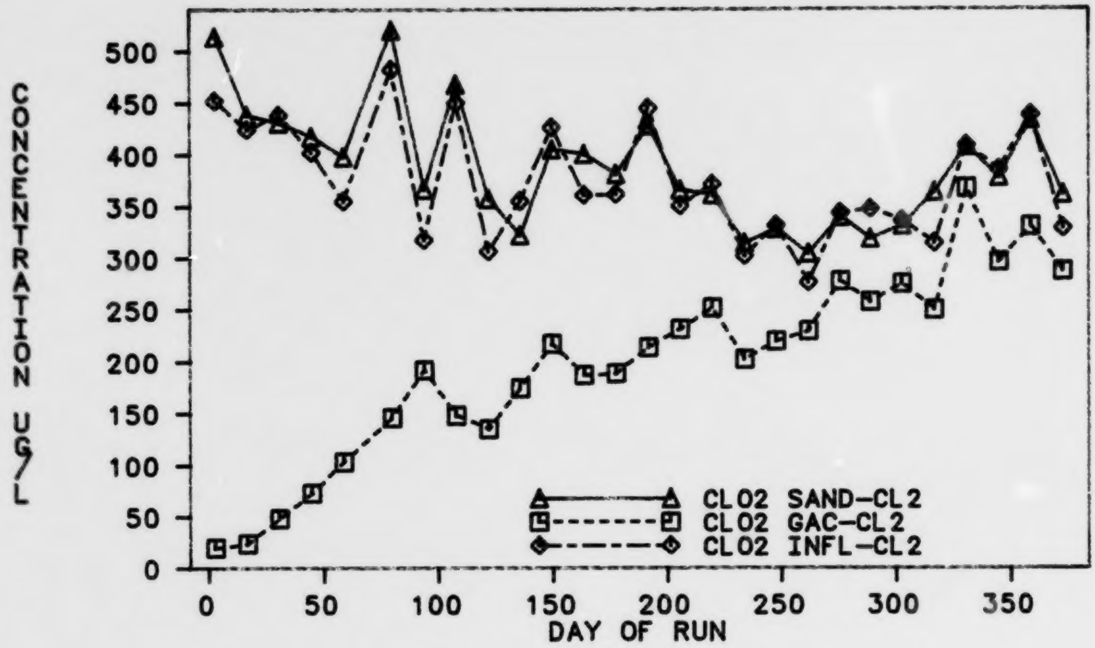


Figure 46. TOX-CL$_2$ and TOX-NH$_2$CL Breakthrough Profiles for the Ozone Process Stream.



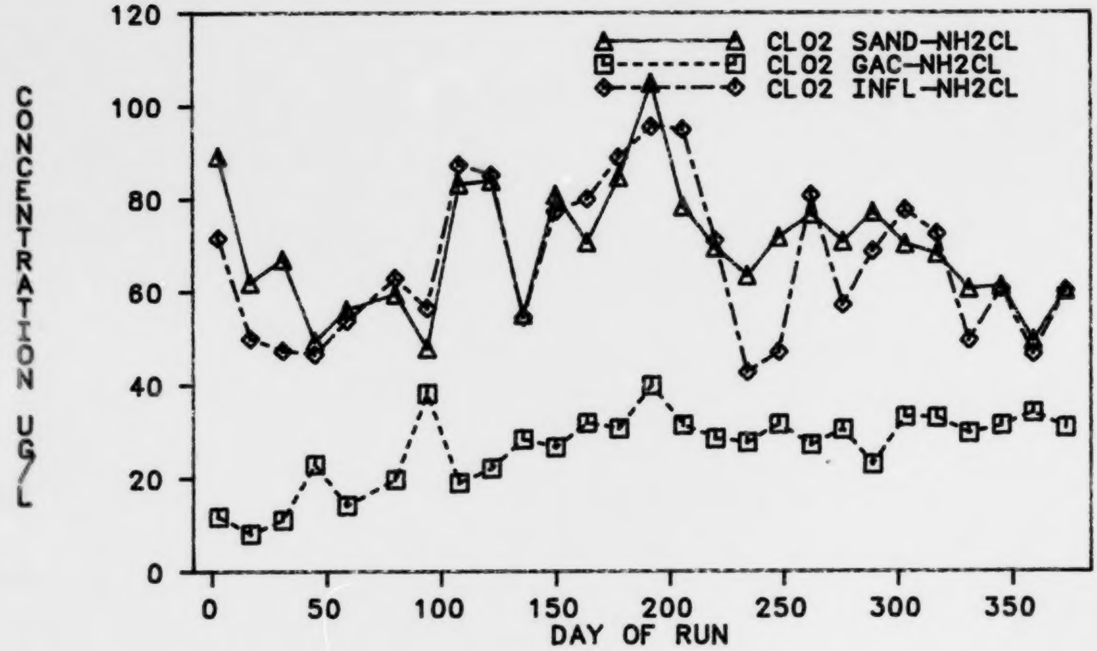


Figure 47. TOX-CL_2 and TOX-NH_2CL Breakthrough Profiles for the Chlorine Dioxide Process Stream.

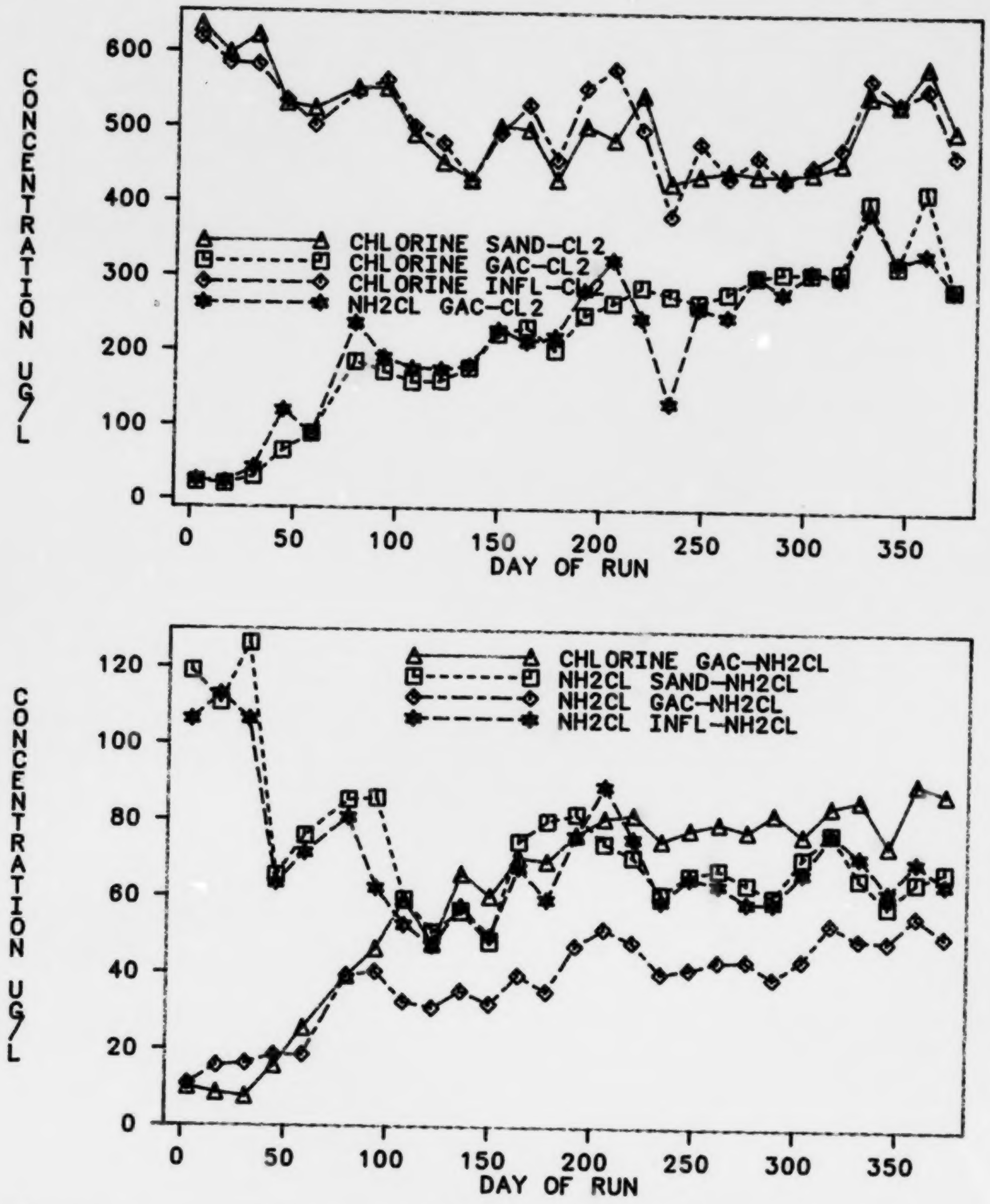


Figure 48. TOX-CL$_2$ and TOX-NH$_2$CL Breakthrough Profiles for the Chlorine and Chloramine Process Streams.

$CHBr_3$ present. Thus the trends observed for the total trihalomethane data presented are primarily that of chloroform.

As expected, the highest levels of THMs were observed for the chlorine process stream with the lowest levels being observed for the ozone, nondisinfected, and chlorine dioxide systems. The THM levels observed the influent water of each disinfectant process stream after 30 minutes of disinfectant contact time are compared to that of the nondisinfected process stream in Figure 49. The relatively large increase in THMs observed on day 115 for all process streams except the chlorine process stream was the result of a partially open chlorine valve in the prechlorination line at the inlet of the clarification units. The average influent levels of THMs observed for each process stream were 1.1 ug/l for the ozone stream, 1.3 ug/l for the nondisinfected and chlorine dioxide streams, 4.5 ug/l for the chloramine stream, and 34 ug/l for the chlorine stream. Thus after 30 minutes of disinfectant contact time an average of 33 ug/l THMs was produced by chlorination while 3 ug/l was produced by chloramination. However, as discussed in the previous section on TOX, an evaluation of the effect of the pulsed ammonia hydroxide feed on the production of THMs indicated that essentially all of the THMs produced in the chloramine system resulted from an estimated 4 seconds of contact with free chlorine. With 30 minute chloramine residuals of 1.6 and 1.4 mg/l for the original and the premixed chloramine systems, respectively, and a water temperature of 10°C, a THM level of 3.6 ug/l was observed for the original chloramine stream while only 0.7 ug/l was observed for both the premixed chloramine system and the nondisinfected influent. This evaluation was performed in duplicate and was again performed after a four month interval at a water temperature of 20°C with similiar results. Thus, this evaluation indicates that properly generated chloramines are just as effective as chlorine dioxide and ozone in minimizing the formation of THMs during disinfection. It is interesting to note, that unlike TOX, there were no THMs formed by the reaction of the 0.1-0.2 mg/l of free chlorine which was incumbent in the chlorine dioxide system. this may be attributable to the differences in the reaction rates of THM and TOX precursors as indicated in the previous section.

As indicated in the previous section on TOX, a second post operational period evaluation was conducted on the ozone process stream in order to determine if the gas purging inherent in the ozone contactor removed any volatile organics. The ozone contactor was operated with the ozone generator "on" and "off" as described in the section on TOX, with an influent concentration of 0.7 ug/l, there was essentially no change observed in the level of THMs with either the ozone generator "on" or "off". Similiar results were observed for 1,2-dichloroethane at the 0.1 ug/l level. Thus, there were no volatile organics lost at the levels indicated across the ozone contactor.

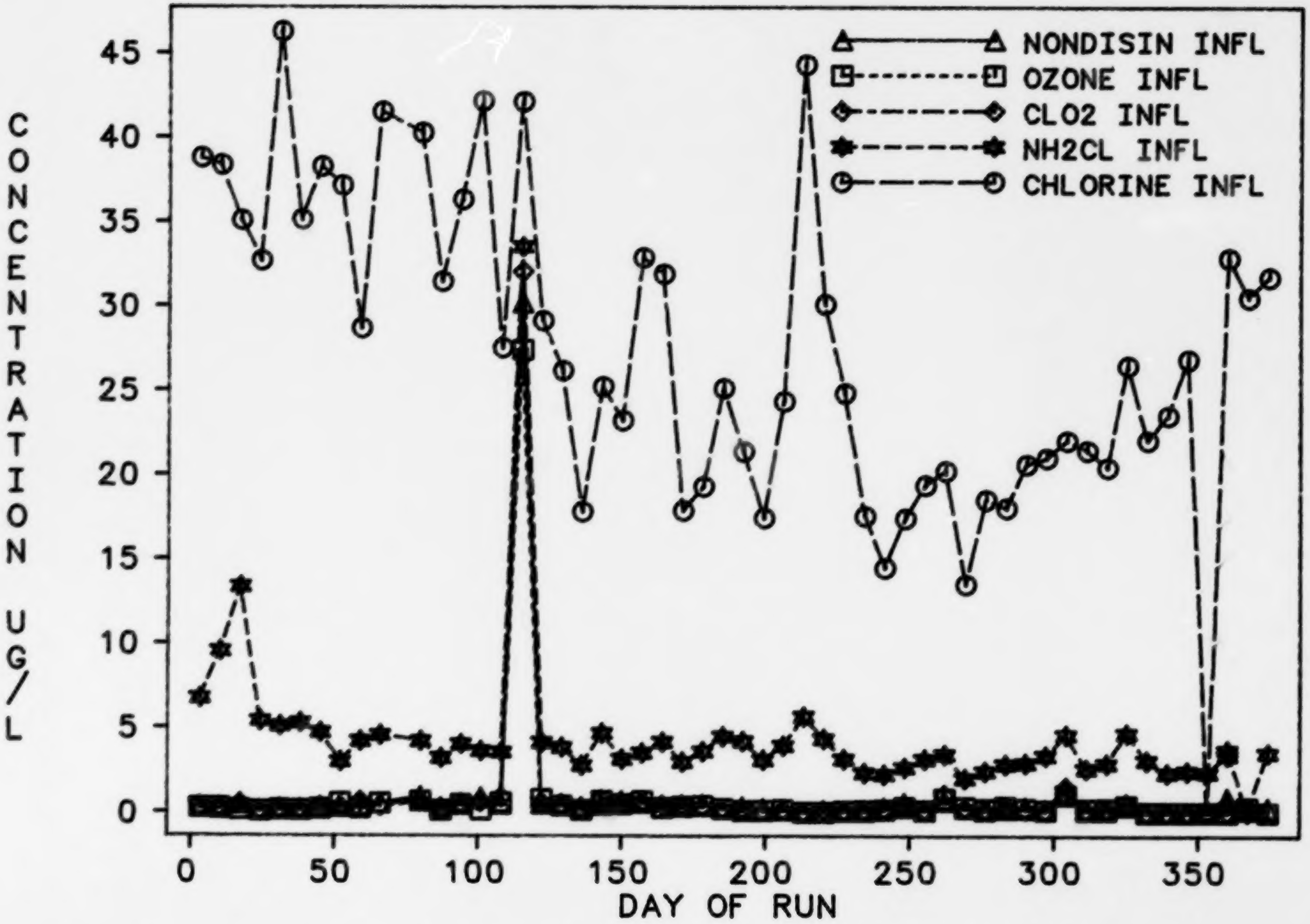


Figure 49. Comparison of the THM-I Influent Levels for each Process Stream.

The THM levels observed in the sand column effluent of each process stream are compared in Figure 50. As might be expected, the levels observed for the nondisinfected, ozone, chlorine dioxide, and chloramine streams were essentially the same as those of their respective influents with average THM levels of 1.5, 1.0, 1.5, and 6.5 ug/l, respectively. On the other hand, the average level of THMs observed in the effluent of the sand column of the chlorine stream increased 13 ug/l to the 50 ug/l level. This increase resulted from additional contact time with free chlorine in the sand column which was estimated to be about 18.4 minutes based upon the volume above the sand bed and the void volume in the sand bed.

The levels of THMs observed in the effluents of the GAC and GAC duplicate columns of each process stream are compared in Figure 51. These columns exhibited essentially duplicate results in each process stream with the highest effluent concentrations being observed for the chlorine stream due to its higher influent concentration followed by that of the chloramine stream respective of its influent concentration. The reductions in THM concentration observed for each GAC column of each process stream are depicted in Figure 52. As was indicated for TOX, the highest THM influent concentration procuded the greatest THM loading, and, it also produced the greatest level of desorption after saturation. Again, it was the lowest influent concentration which produced the lowest effluent concentration indicating that the optimum GAC system relative to the removal of THMs would be the nondisinfected, ozone, and chlorine dioxide systems or a properly generated chloramine system.

The breakthrough profiles of THMs through the GAC and GAC duplicate columns of each process stream are presented in Figures 53-57. Due to the low concentrations (<1 ug/l) observed in the influents and effluents of the nondisinfected, ozone, and chlorine dioxide GAC columns, it is difficult to determine the exact level of removal prior to saturation. However, a definite increase in effluent concentration above that of the influent concentration was observed on day 120 for each of these GAC columns at about the 1 ug/l level. In contrast, the chloramine GAC columns reached a state of saturation on day 90 at the 5 ug/l level while the chlorine GAC columns also reached saturation on day 90, but at the 70 ug/l level. As was observed for TOX, these THM data further illustrate that while a higher influent concentration produced a higher level of GAC loading, a higher influent concentration does not appear to be directly associated with a shorter GAC bed life.

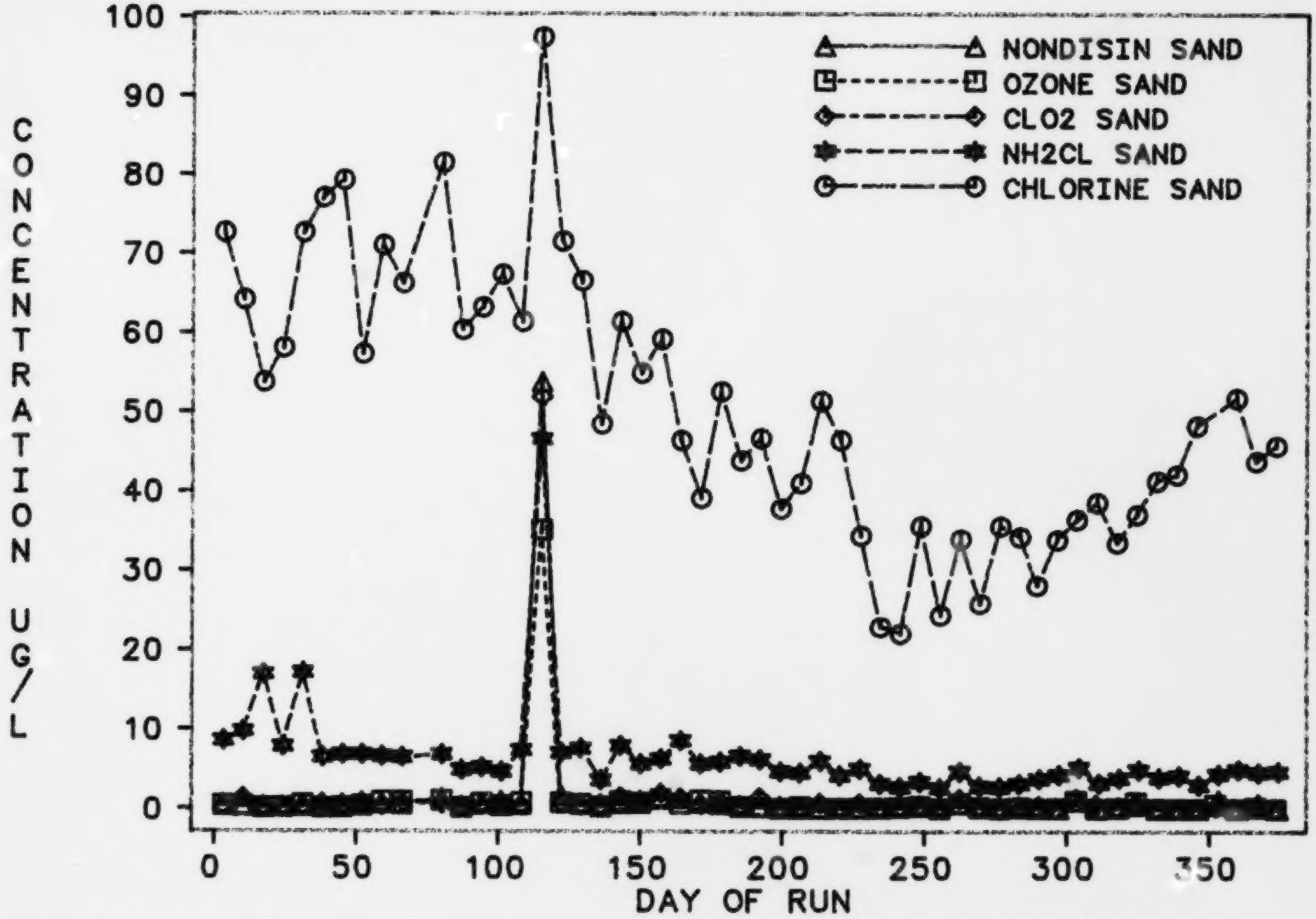
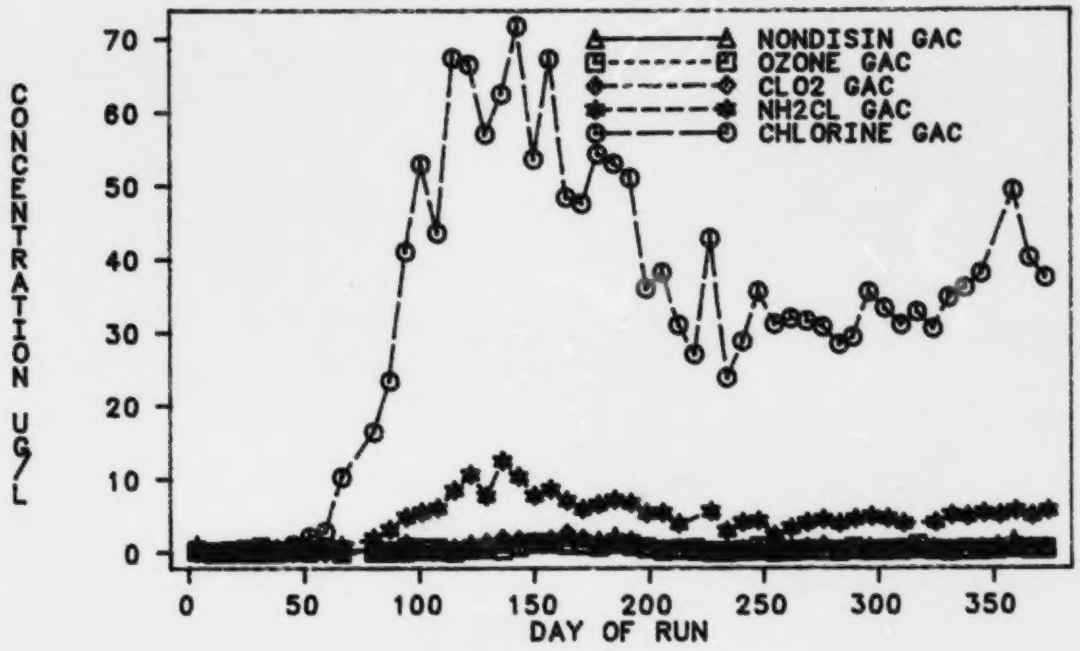


Figure 50. Comparison of the THM-I Sand Effluent Levels for each Process Stream.



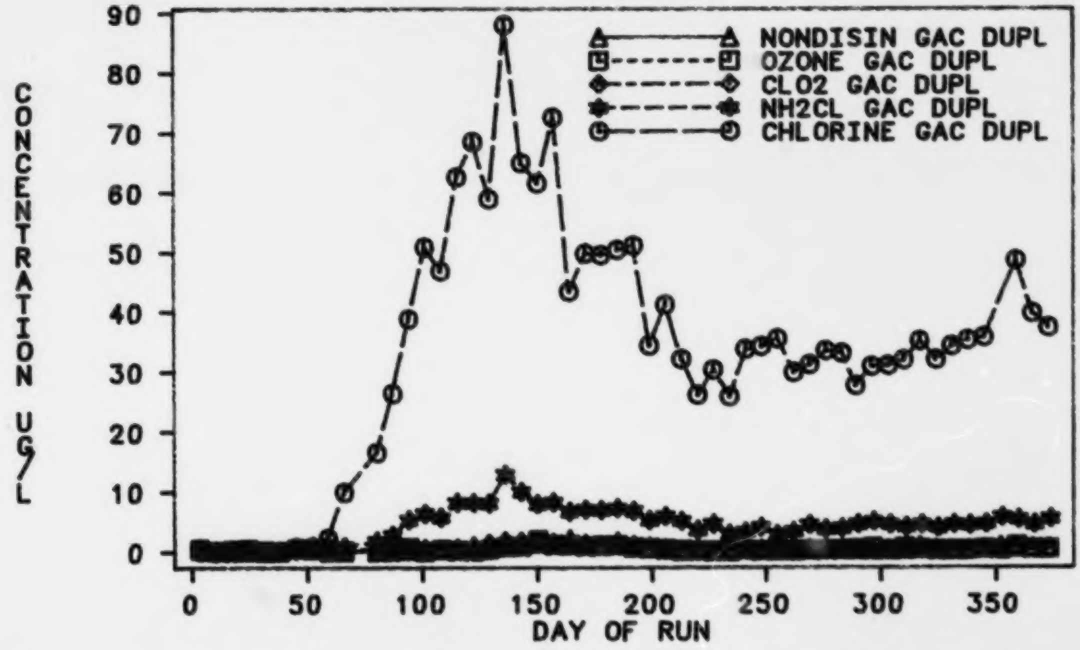


Figure 51. Comparison of the THM-I GAC and GAC Duplicate Effluent Levels for each Process Stream.

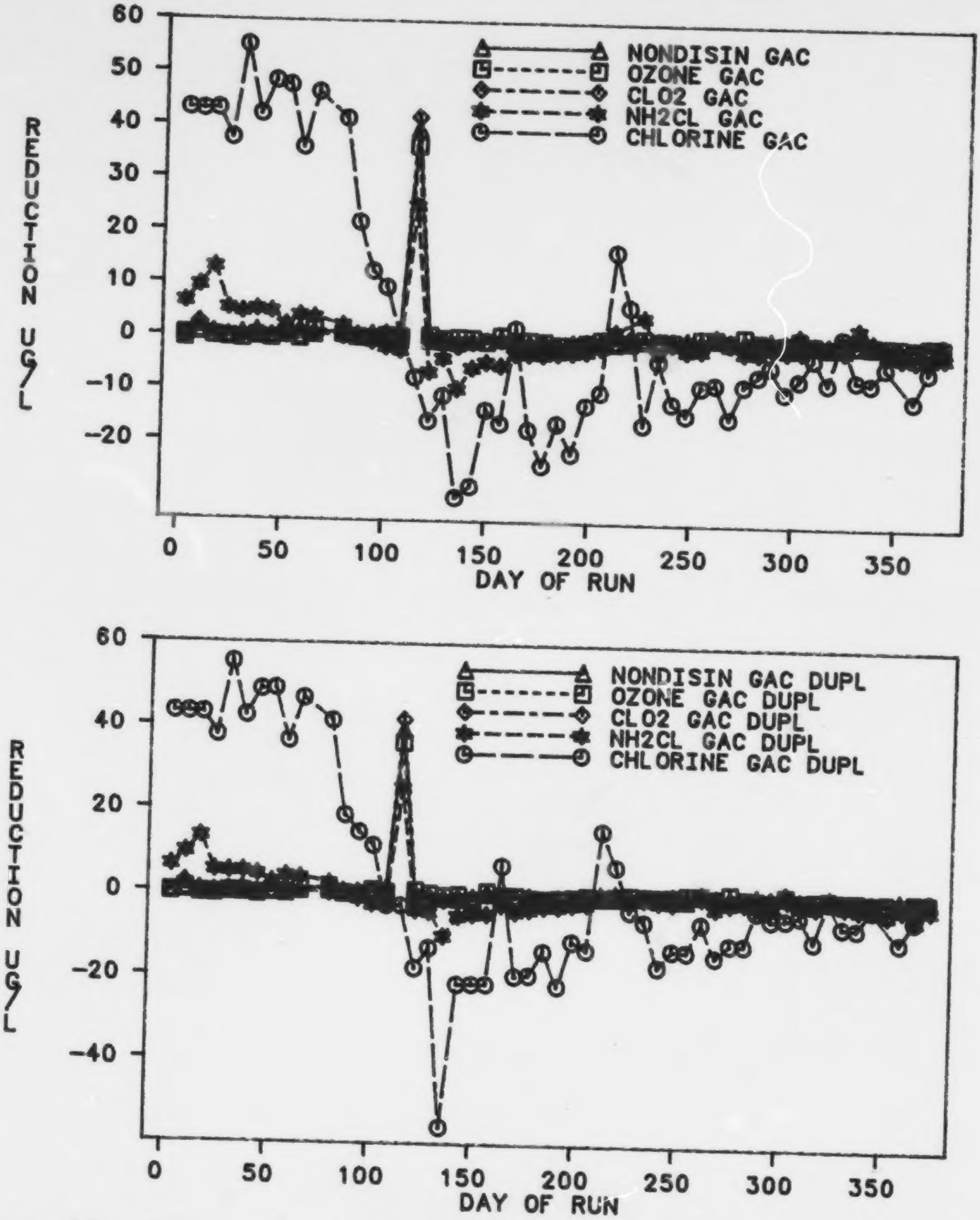


Figure 52. Comparison of the THM-I Reductions Observed Across each GAC and GAC Duplicate Column.

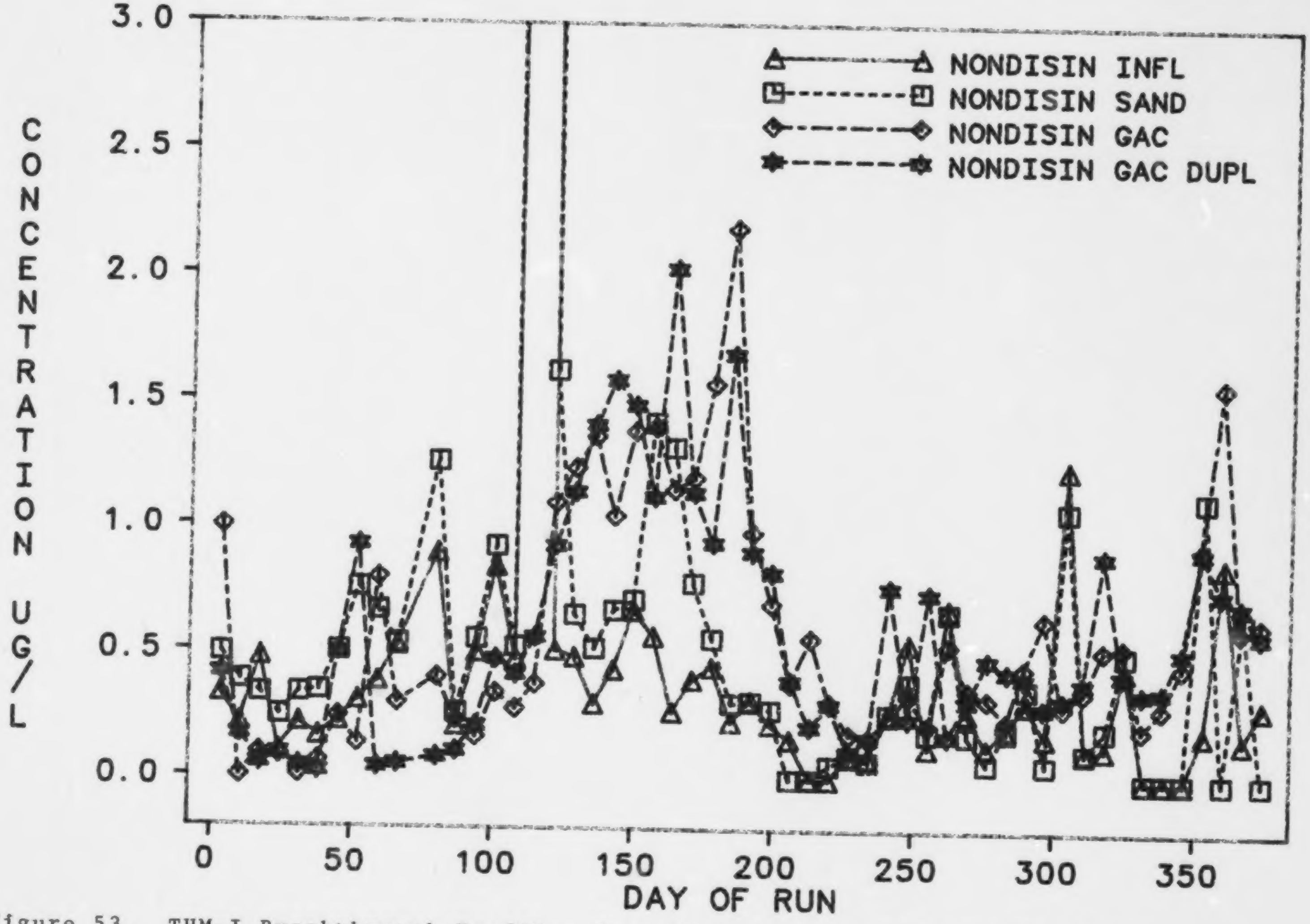


Figure 53. THM-I Breakthrough Profiles for the Nondisinfected Process Stream.

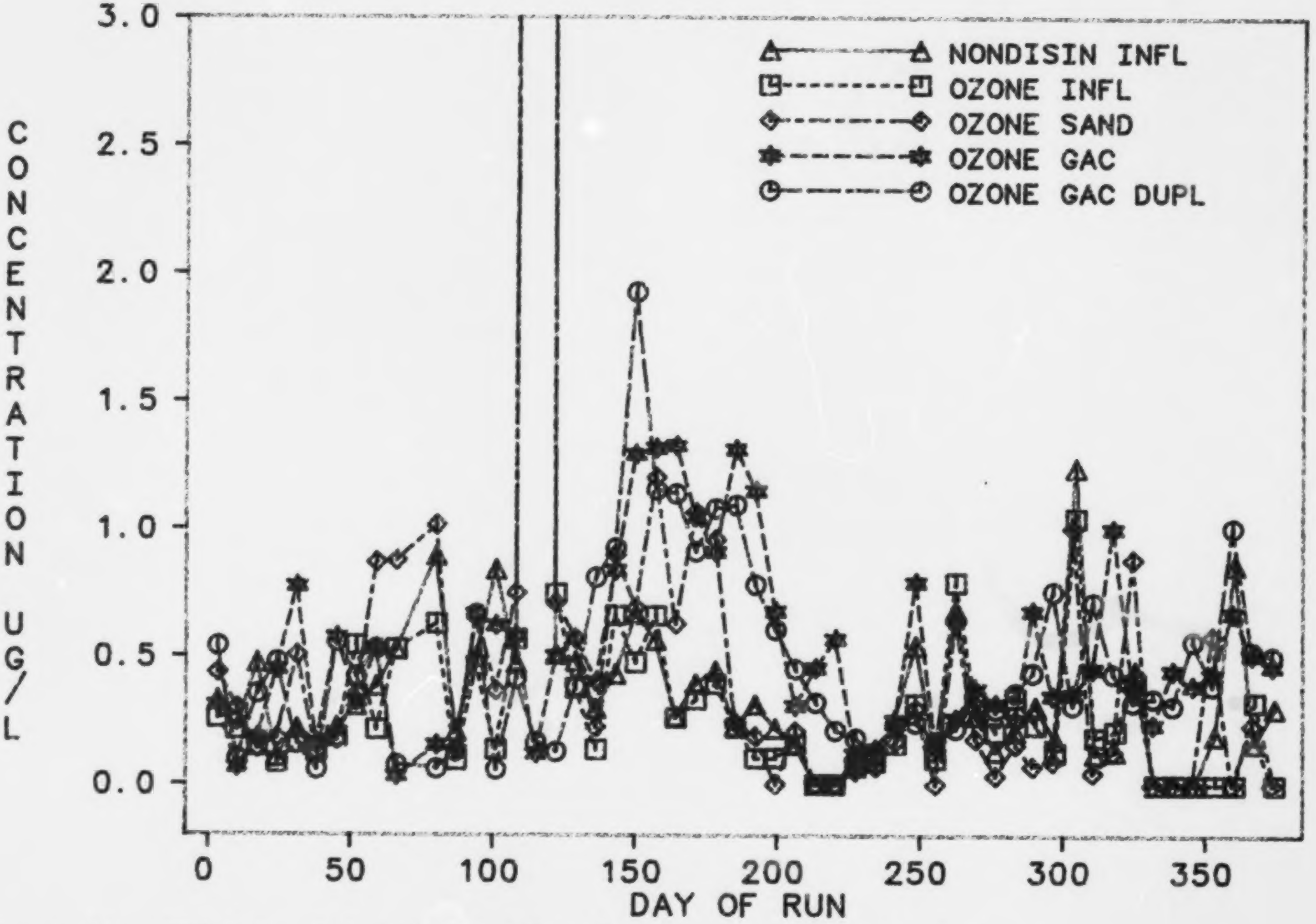


Figure 54. THM-I Breakthrough Profiles for the Ozone Process Stream.

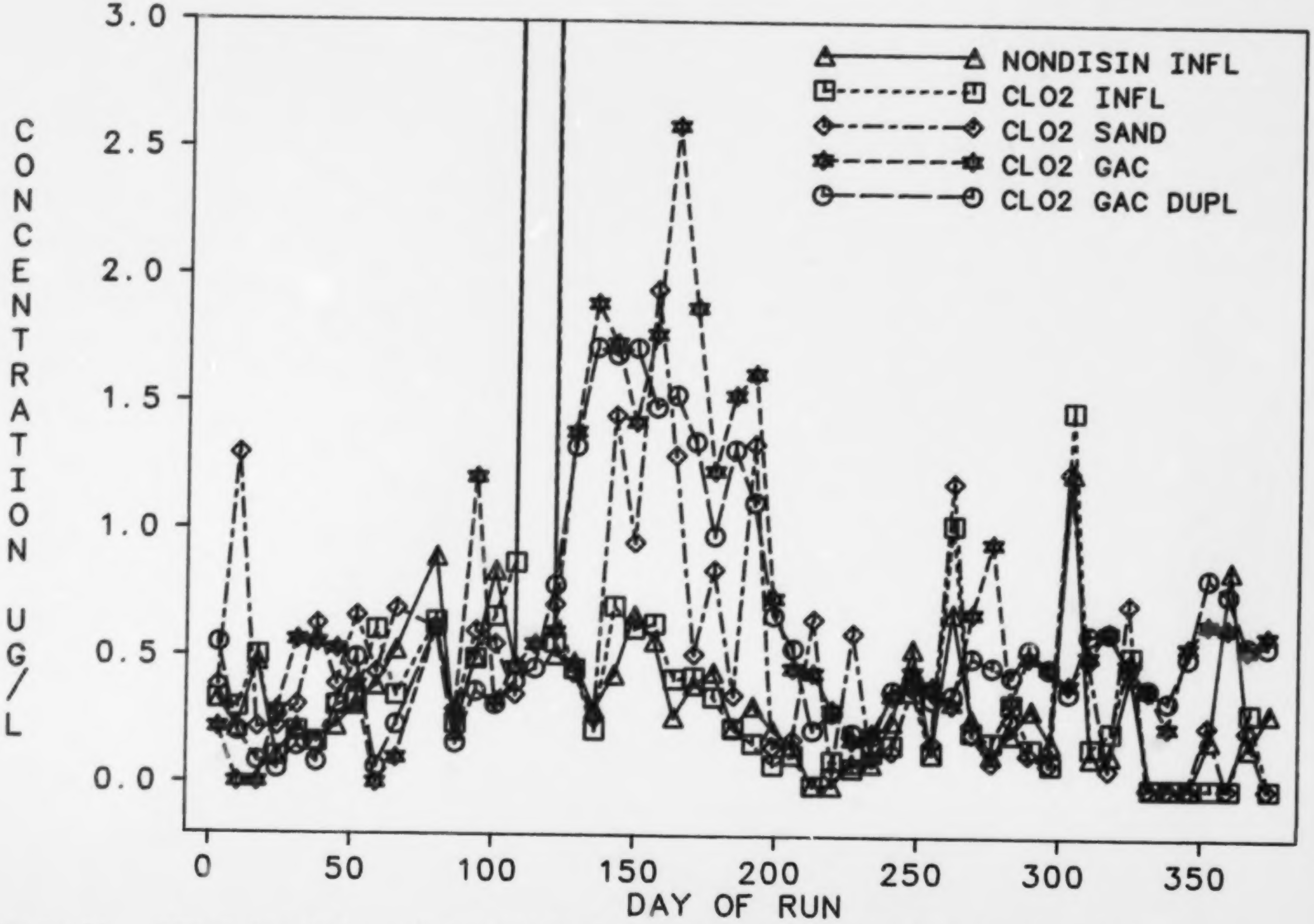


Figure 55. THM-I Breakthrough Profiles for the Chlorine Dioxide Process Stream.

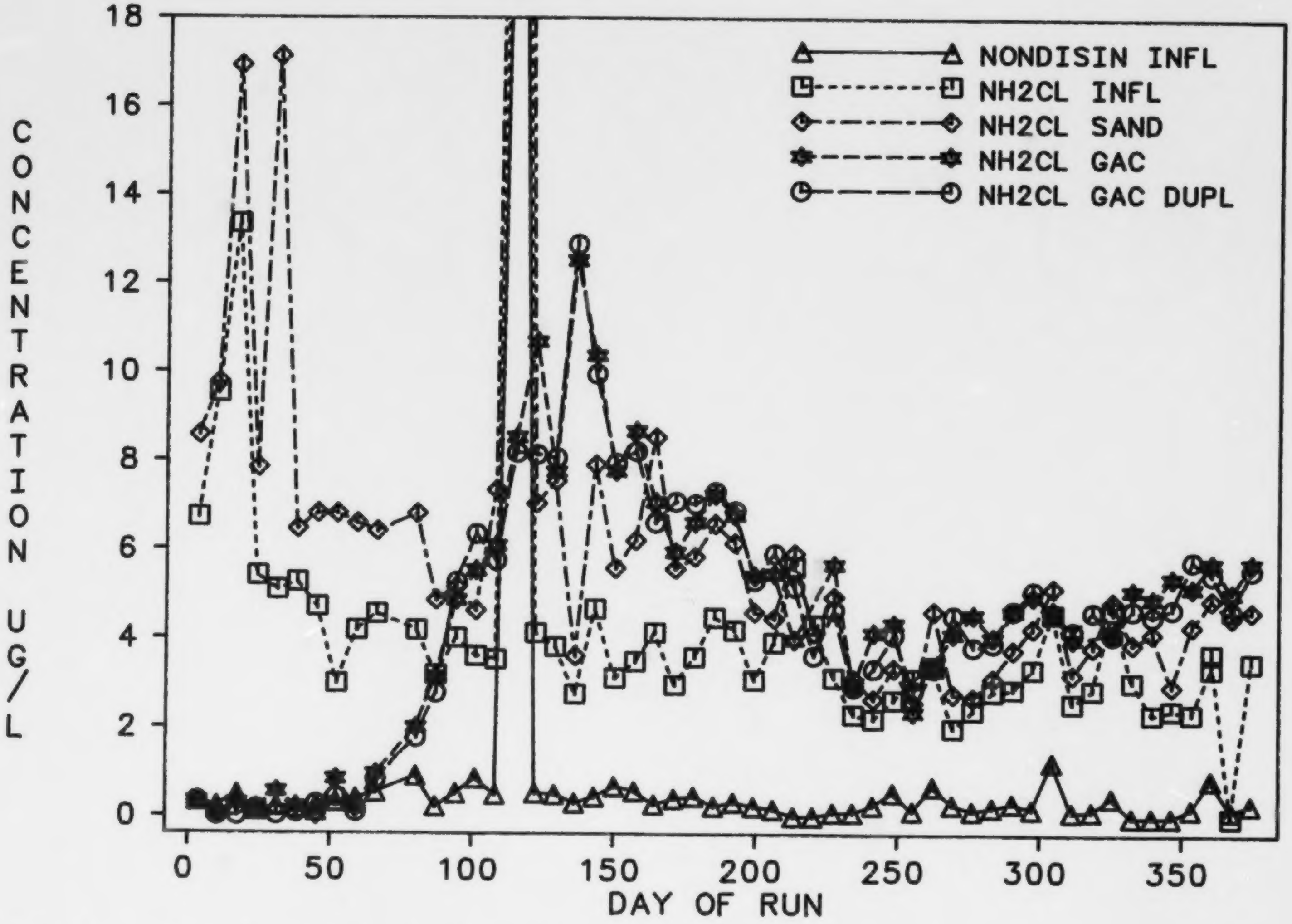


Figure 56. THM-I Breakthrough Profiles for the Chloramine Process Stream.

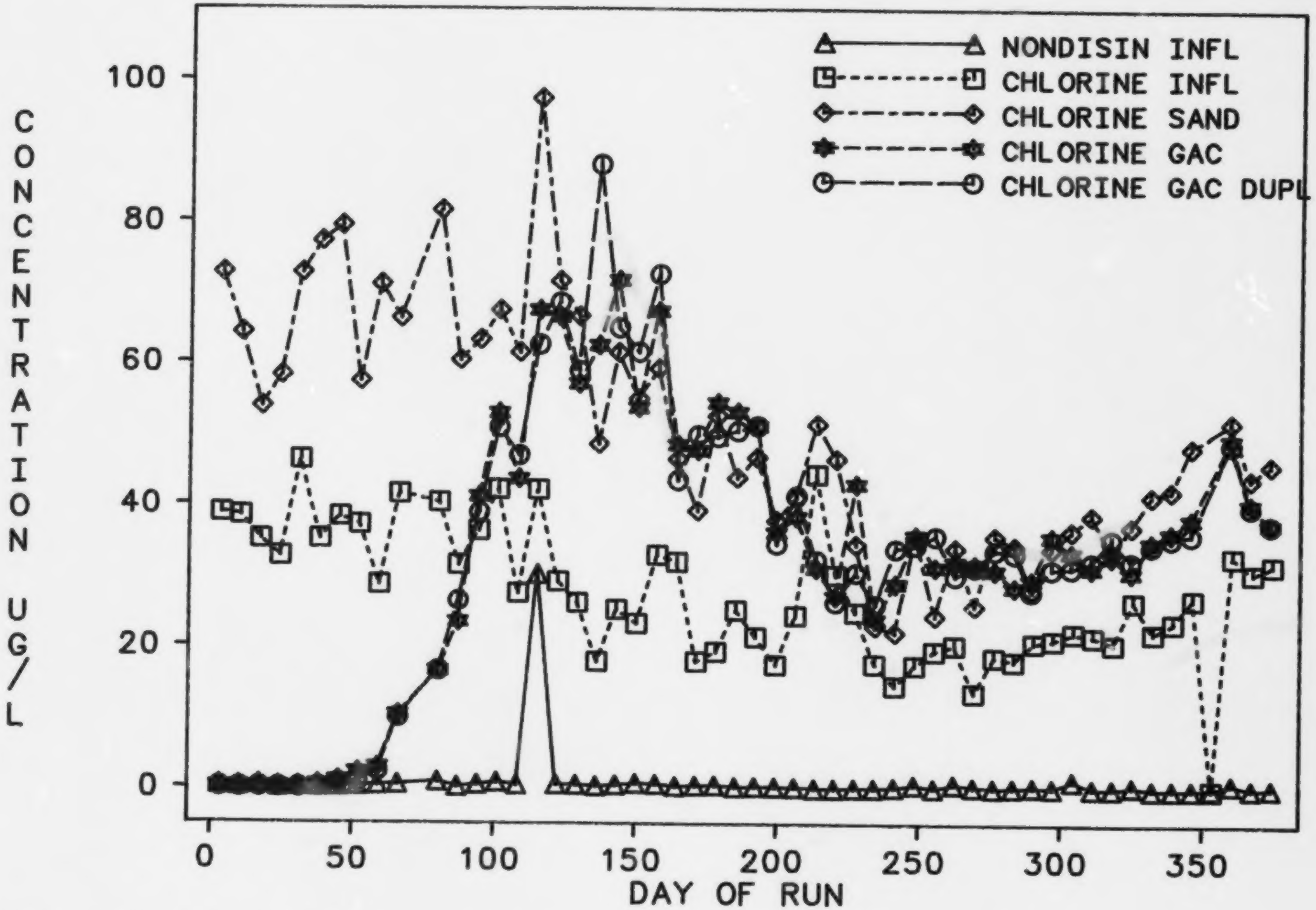


Figure 57. THM-I Breakthrough Profiles for the Chlorine Process Stream.

TERMINAL THMs --

The terminal THM levels observed for those samples treated with free chlorine (THM-Cl_2) are indicative of the total THM formation potential while terminal THM levels observed for those samples treated with chloramines (THM-NH_2Cl) exhibit the relatively nonreactive nature of chloramines with THM precursors. A comparison of the average terminal THM-Cl_2 levels observed for each sample location along with there average instantaneous THM levels are presented in Figure 58. Thirty minutes of disinfectant contact with ozone and chlorine dioxide produced average THM precursor reductions of 121 ug/l (45%) and 113 ug/l (42%), respectively. Interestingly enough, THM precursor levels in the chlorine influent were consistantly less than that of the nondisinfectant influent with an average reduction of 46 ug/l (17%). The actual THM-Cl_2 data for the nondisinfected and chlorine streams can be seen in the upper portion of Figure 65 which is presented later in this section. The only difference in the chlorine dosages for these two locations was that the chlorine influent was dosed with approximately 3 mg/l of free chlorine followed by an additional 4 mg/l dosage approximately 3.5 hrs. later, while the nondisinfectant influent was dosed only once with 7 mg/l of free chlorine. THM precursor reductions of 54 ug/l (20%) and 18 ug/l (12%) were observed across the sand columns of the nondisinfected and ozone streams, respectively. As was indicated for TOX precursors, these reductions can be attributed to biodegradation of THM precursors. Similiar THM precursor levels were observed for the nondisinfected and chlorine streams after GAC filtration which averaged 101 and 107 ug/l, respectively. Those for the chlorine dioxide and chloramine streams were slightly lower at 89 and 92 ug/l, respectively, while the lowest levels of THM precursors were observed in the effluent of the ozone GAC column which averaged 50 ug/l. These consistantly lower THM precursor levels in the effluent of the ozone GAC column can be observed in Figure 59 which compares the GAC effluent levels of THM-Cl_2 for all process streams.

The average terminal THM-NH_2Cl level observed for each sampling location are compared in Figure 60 along with each locations average instantaneous THM level. As with TOX-NH_2Cl, these average THM-NH_2Cl levels are primarily indicative of the nonreactivity of chloramines as opposed to the removal of THM precursors. The lowest average terminal THM-NH_2Cl level was observed for the ozone system followed by the chlorine dioxide system, the nondisinfected system, and the chloramine system for the influent, sand effluent, and GAC effluent sampling locations. The highest THM-NH_2Cl levels for the GAC effluent sampling locations were observed for the chlorine system as depicted in Figure 61. The terminal THM-NH_2Cl levels for the ozone, chlorine dioxide, and nondisinfected GAC effluents were for the most part

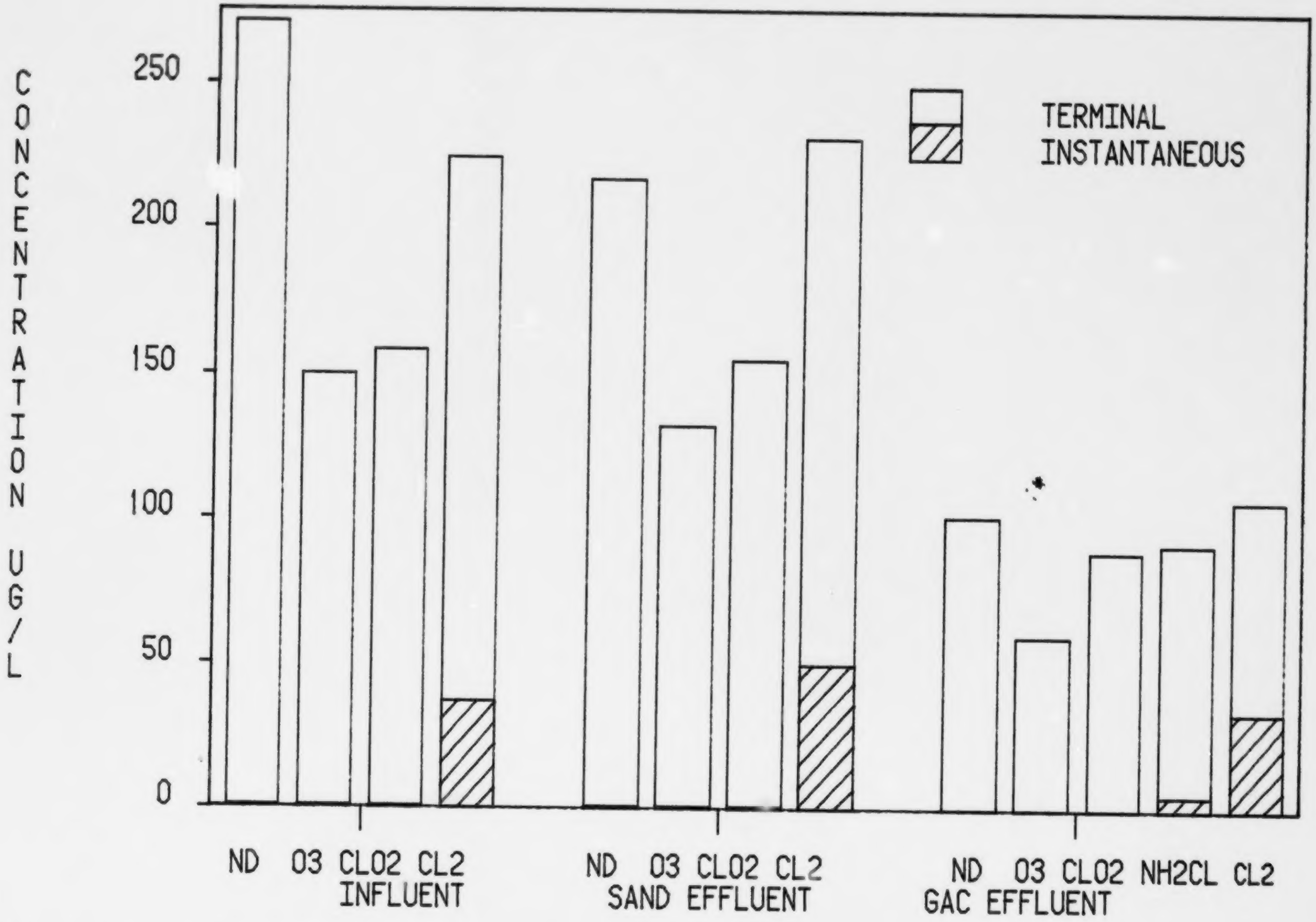


Figure 58. Average Terminal THM-CL_2 Levels After the Addition of Free Chlorine and Storage for 5 Days at 28°C.

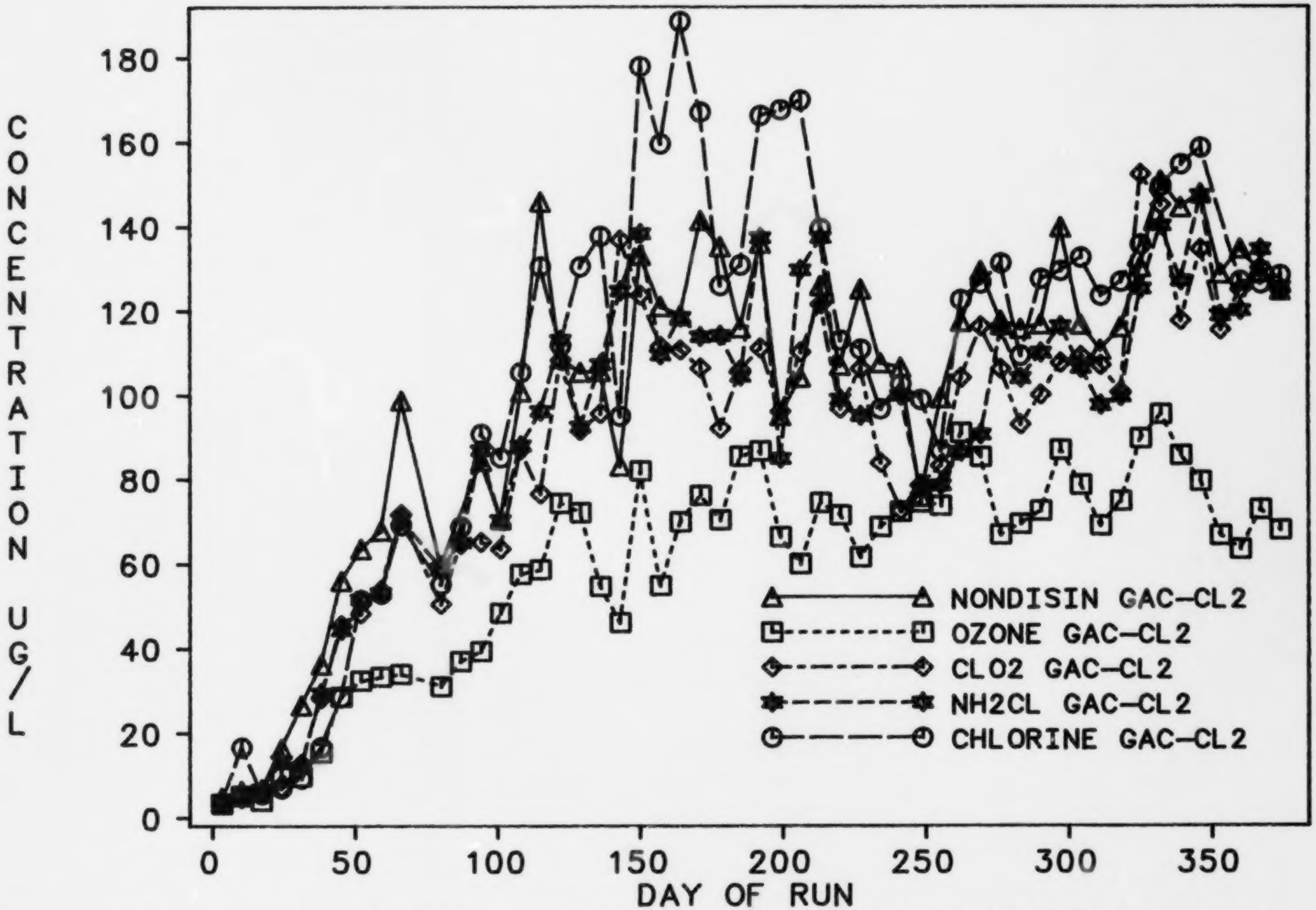


Figure 59. Comparison of the THM-CL$_2$ GAC Effluent Levels for each Process Stream.

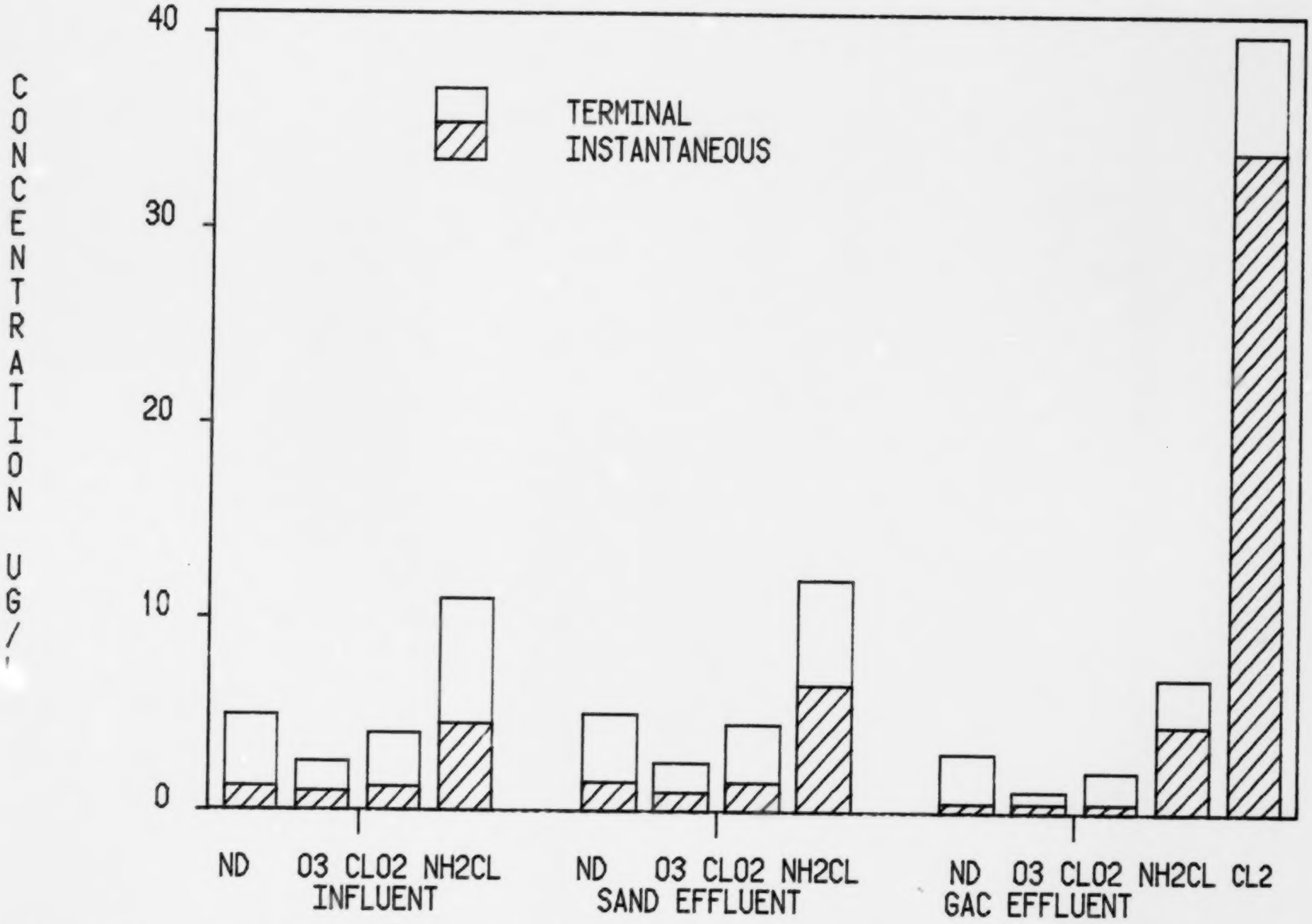


Figure 60. Average Terminal THM-NH_2CL Levels After the Addition of Monochloramine and Storage for 5 days at 28°C.

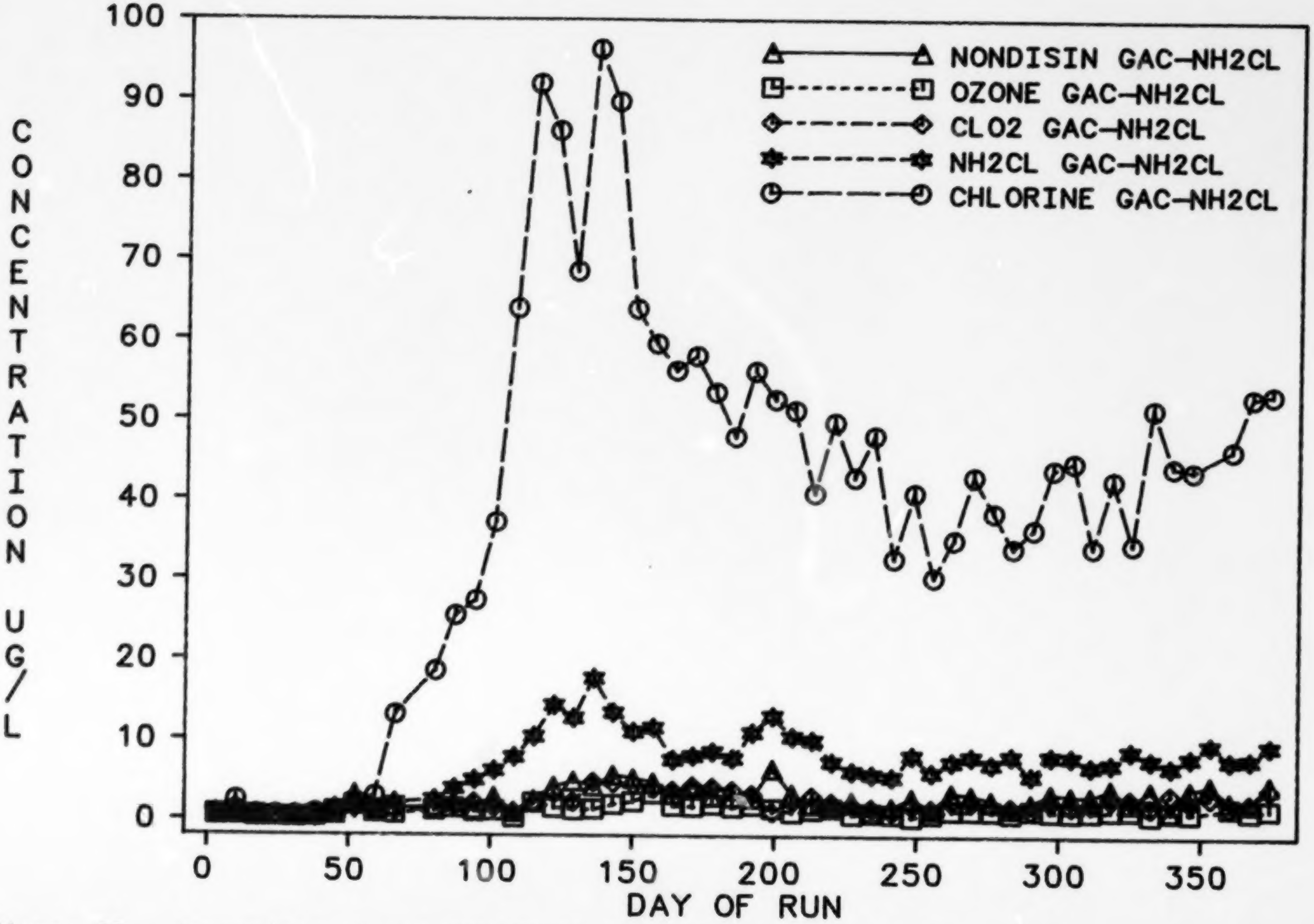


Figure 61. Comparison of the THM-NH_2CL GAC Effluent Levels for each Process Stream.

below 5 ug/l throughout the entire operational period while those for the chloramine GAC effluents were below 10 ug/l. Some portion of these higher levels observed in the chloramine GAC effluent can be attributable to the unusually high instantaneous THM levels which resulted from a short term contact with free chlorine as previously discussed.

The terminal THM-Cl$_2$ and THM-NH$_2$Cl breakthrough profiles for the GAC columns of each process stream are presented in Figures 62-65. Both of the terminal THM-Cl$_2$ and THM-NH$_2$Cl levels in the combined GAC effluents of the nondisinfectant stream reached a "steady state" condition on day 100. However, the level at which "steady state" was reached for THM-Cl$_2$ was 120 ug/l with an average reduction of 147 ug/l after day 100 while that for THM-NH$_2$Cl was 2 ug/l with an average reduction of 2 ug/l after day 100. For the ozone stream, THM-Cl$_2$ reached "steady state" on day 150 at the 75 ug/l level with an average reduction of 61 ug/l after day 150 while THM-NH$_2$Cl reached this condition almost immediately at the 1-2 ug/l level with an average reduction of 1 ug/l. Similiar conditions were observed for the chlorine dioxide stream with THM-Cl$_2$ reaching "steady state" on day 150 at the 110 ug/l level with an average reduction of 37 ug/l after day 150. A "steady state" condition was reached on day 100 for THM-NH$_2$Cl in the chlorine dioxide stream at the 2 ug/l level with an average reduction of 2 ug/l after day 100. The GAC effluents of both the chloramine and chlorine streams reached a "steady state" condition on day 150 at the 125 ug/l level for THM-Cl$_2$ indicating that there was no removal of THM precursors via disinfection with chloramines. While the combined GAC effluents of the chlorine system exhibited an average THM-Cl$_2$ reduction of 75 ug/l after day 150, an average THM-Cl$_2$ increase of 103 ug/l was observed for the chloramine stream over the THM-NH$_2$Cl levels of its influent. For THM-NH$_2$Cl, the combined GAC effluents of both the chloramine and chlorine streams reached "steady state" on day 100. The chloramine stream reached "steady state" at the 10 ug/l level with an average reduction of 2 ug/l after day 100 while this condition occurred for the chlorine system at the 90 ug/l level with an average reduction of 166 ug/l after day 100. However, in comparision with the chloramine influent for THM-NH$_2$Cl, the combined GAC effluents of the chlorine system exhibited an average increase of 40 ug/l.

1,2-DICHLOROETHANE (DCE)

The concentration of 1,2-dichloroethane (DCE) in the nondisinfected influent of the pilot column system ranged from below the detection limit to 7 ug/l over the duration of the operational period. Thirty minutes of disinfectant contact time with ozone, chlorine dioxide, chloramines, and chlorine produced no significant change in DCE concentration as was the case for the sand column of each disinfectant process stream as indicated

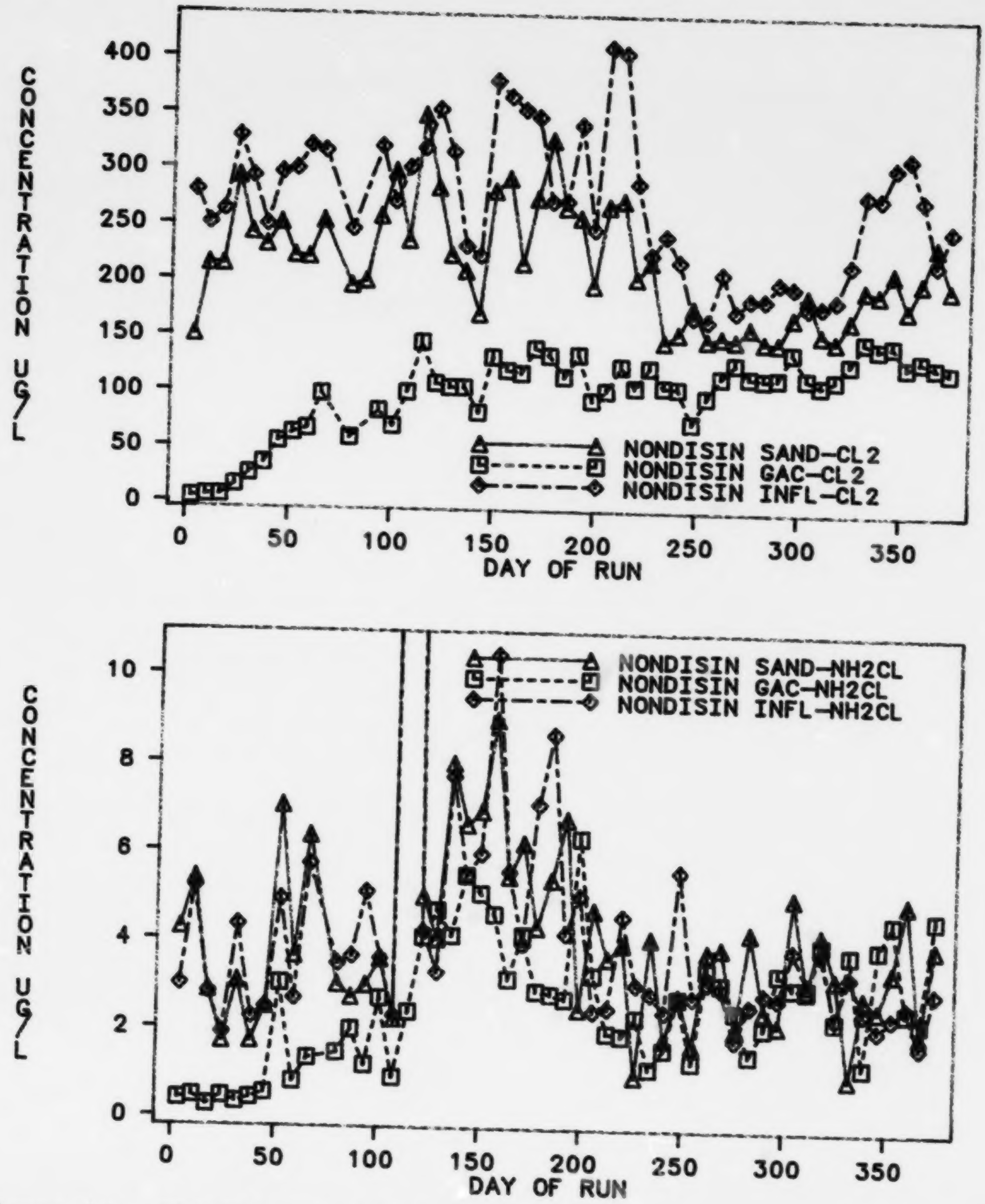
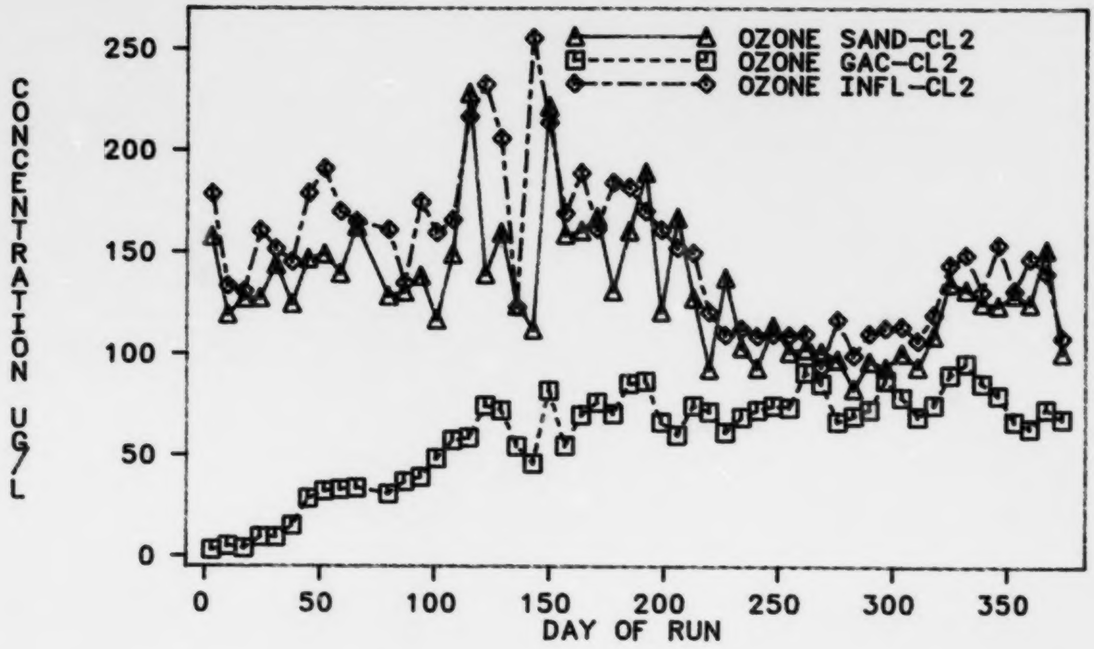


Figure 62. THM-CL_2 and THM-NH_2CL Breakthrough Profiles for the Nondisinfected Process Stream.



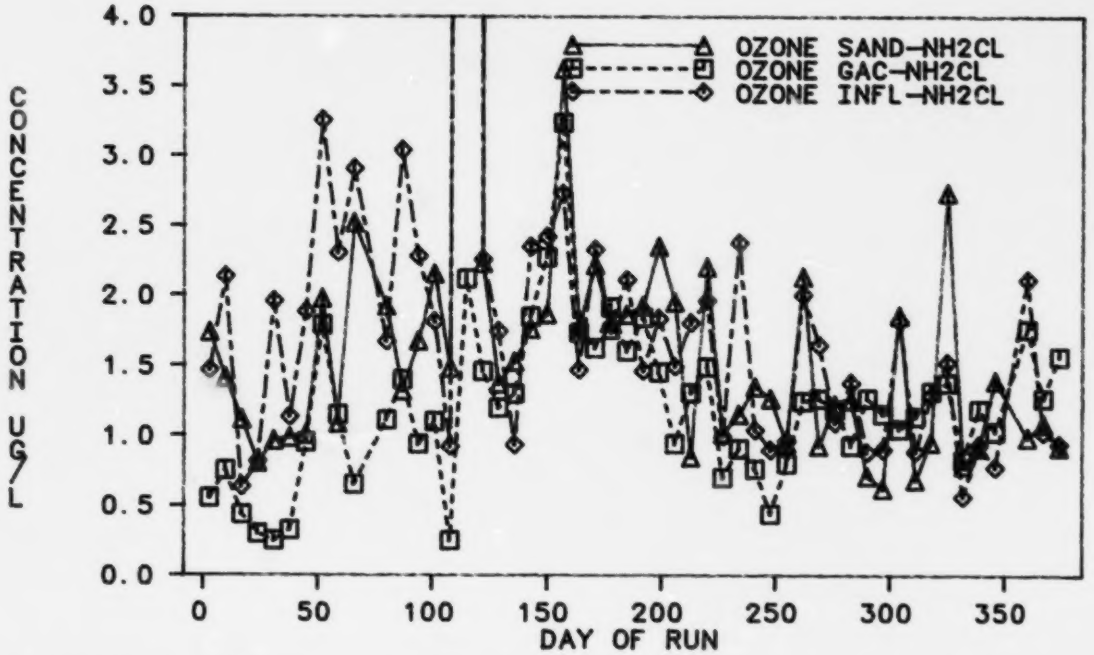


Figure 63. THM-CL_2 and THM-NH_2CL Breakthrough Profiles for the Ozone Process Stream.

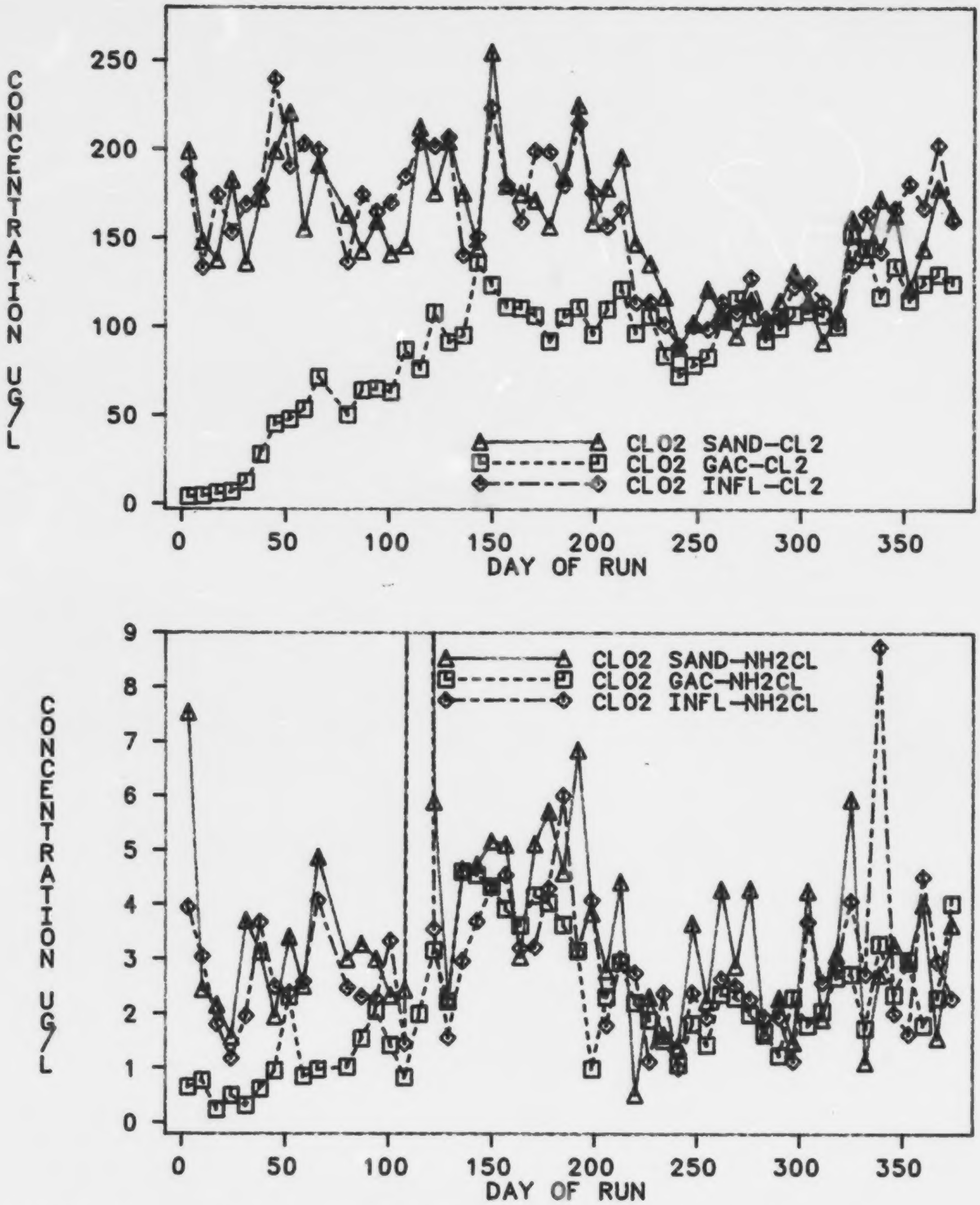
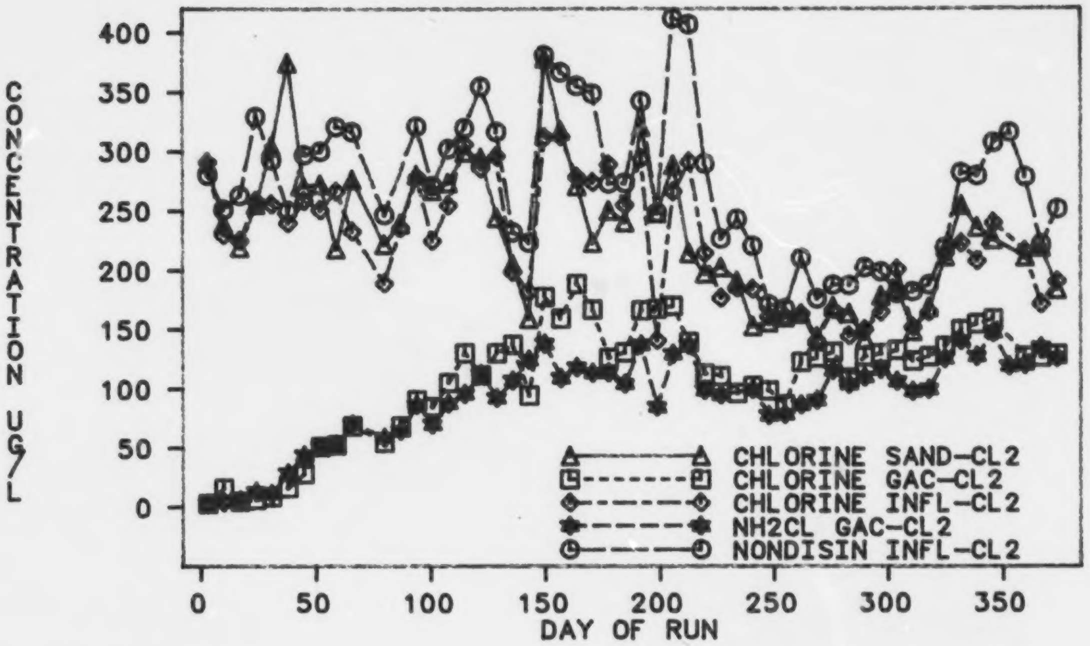


Figure 64. THM-CL_2 and THM-NH_2CL Breakthrough Profiles for the Chlorine Dioxide Process Stream.



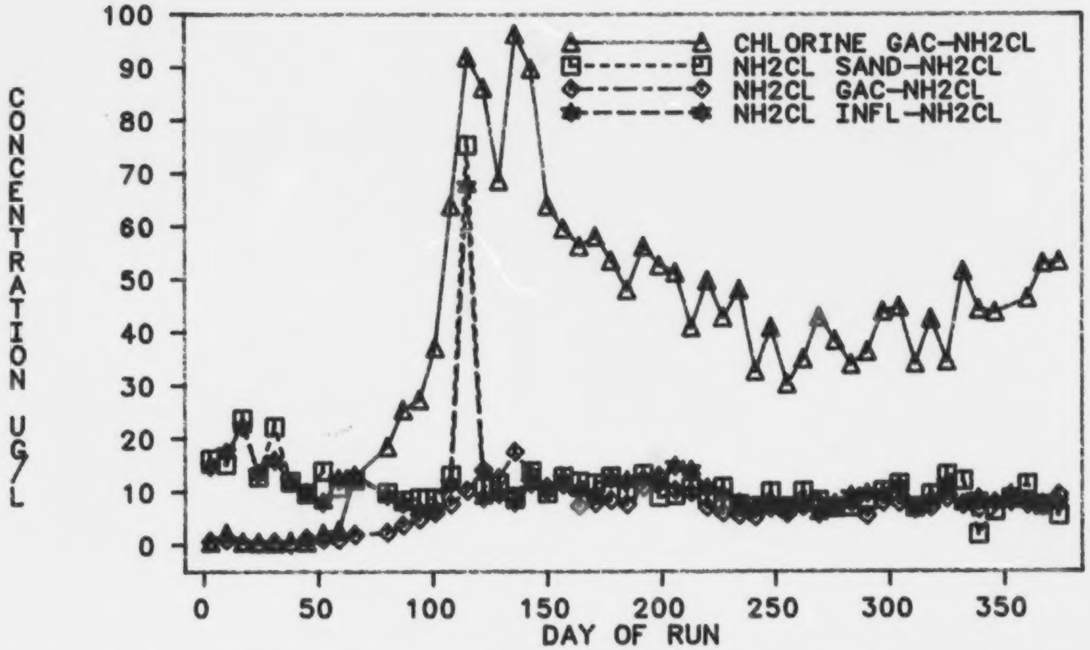


Figure 65. THM-CL_2 and THM-NH_2CL Breakthrough Profiles for the Chlorine and Chloramine Process Streams.

in Figure 66. The DCE concentrations in the effluent of the GAC columns of each process stream are compared in Figure 67. While the effluent concentrations of the nondisinfected, ozone, chlorine dioxide, and chloramine GAC columns were quite similiar, that for the chlorine GAC column was relatively higher after the breakthrough of DCE through the GAC bed. Similiar results were observed for the duplicate GAC columns of each process stream. Because the influent levels of DCE in each process stream were essentially identical, the higher effluent levels of the chlorine GAC columns are believed to have resulted from competative adsorption since the loading of THMs, which are similiar sized molecules, was significantly greater for the GAC columns of the chlorine stream as compared to those of the other process streams.

Typical DCE breakthrough profiles of the GAC columns of the nondisinfected and chlorine streams are presented in Figure 68. Almost identical breakthrough curves were observed for the GAC columns of all process streams with each GAC column reaching saturation about day 90 at the 0.2 ug/l level.

OTHER VOLATILE ORGANICS

The other volatile organics observed in the influent waters over the course of the operational period were dichloromethane, trichloroethylene, 1,1,2-trichloroethane, and carbon tetrachloride. These compounds occurred very infrequently at concentrations below 0.1 ug/l except for one occurrance in which trichloroethylene reached a maximum of approximately 20 ug/l which was undoubtedly the result of a point source discharge into the Mississippi River. Relatively no trichloroethylene was observed in the effluent of the GAC columns indicating some adsorptive capacity for this substance. Because of a lack of extensive data, relatively no conclusions with regard to the effects of the alternative disinfectants or to the removal of these substances by GAC filtration can be drawn.

ATRAZINE

The atrazine concentrations in the nondisinfected influent of the pilot column system ranged from 23-249 ng/l over the one year operational period with an average of 80 ng/l. A profile of these data is presented in Figure 69 and compared to that of the disinfected influent streams after 30 minutes of disinfectant contact time. The influent atrazine concentration was uneffected by chlorine dioxide, chloramine, and free chlorine. However, an average removal of 83% was observed for ozonation. A comparison of the atrazine levels in the effluent of the sand columns is presented in Figure 70. As indicated, there were essentially no

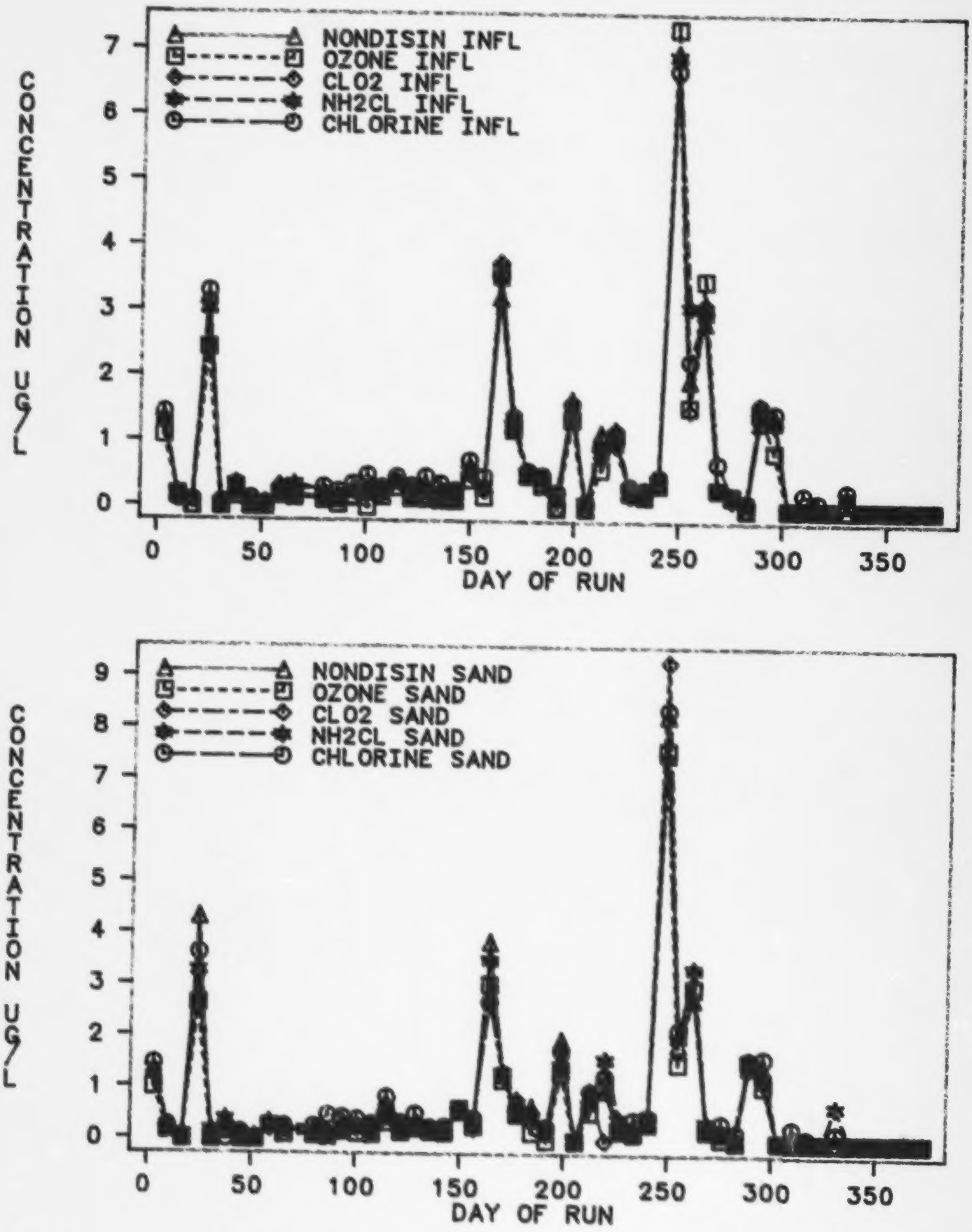


Figure 66. Comparison of the 1,2-dichloroethane Influent and Sand Effluent Levels for each Process Stream.

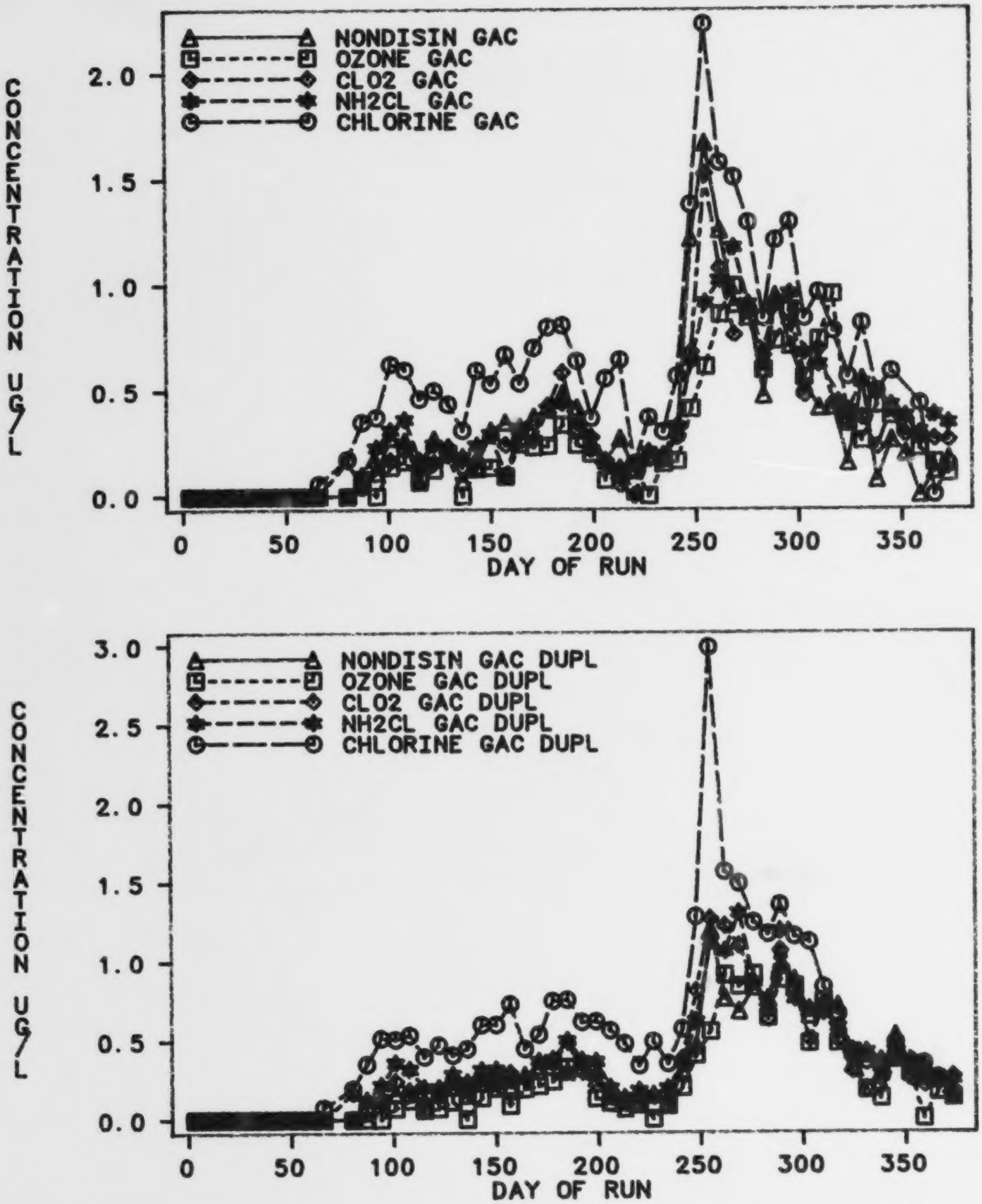
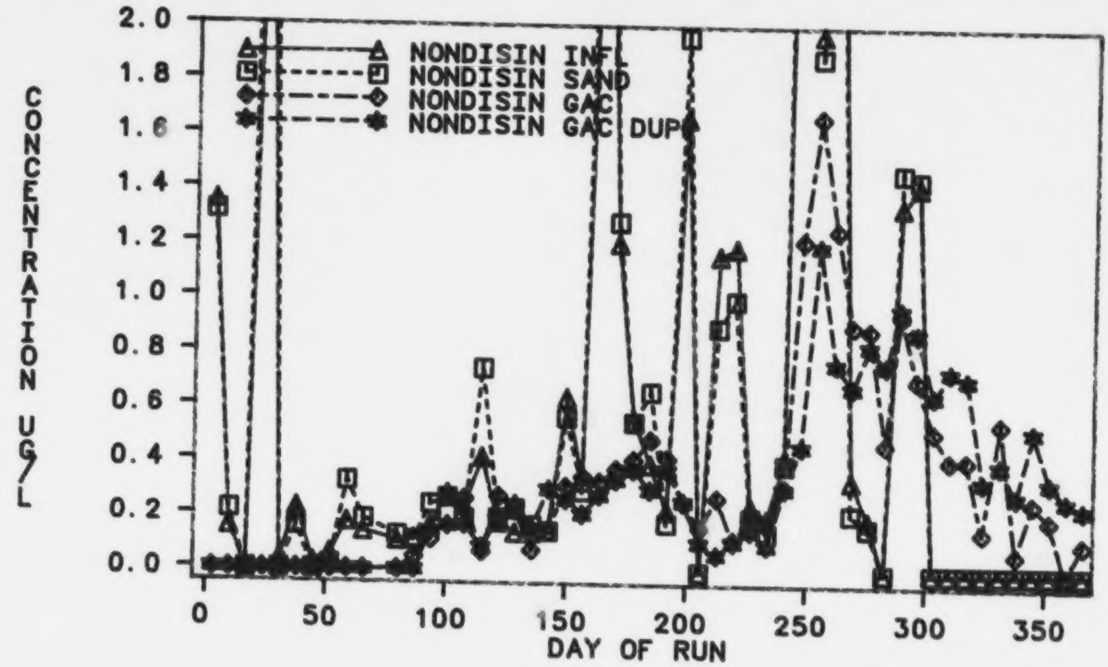


Figure 67. Comparison of the 1,2-dichloroethane GAC and GAC Duplicate Effluent Levels for each Process Stream.



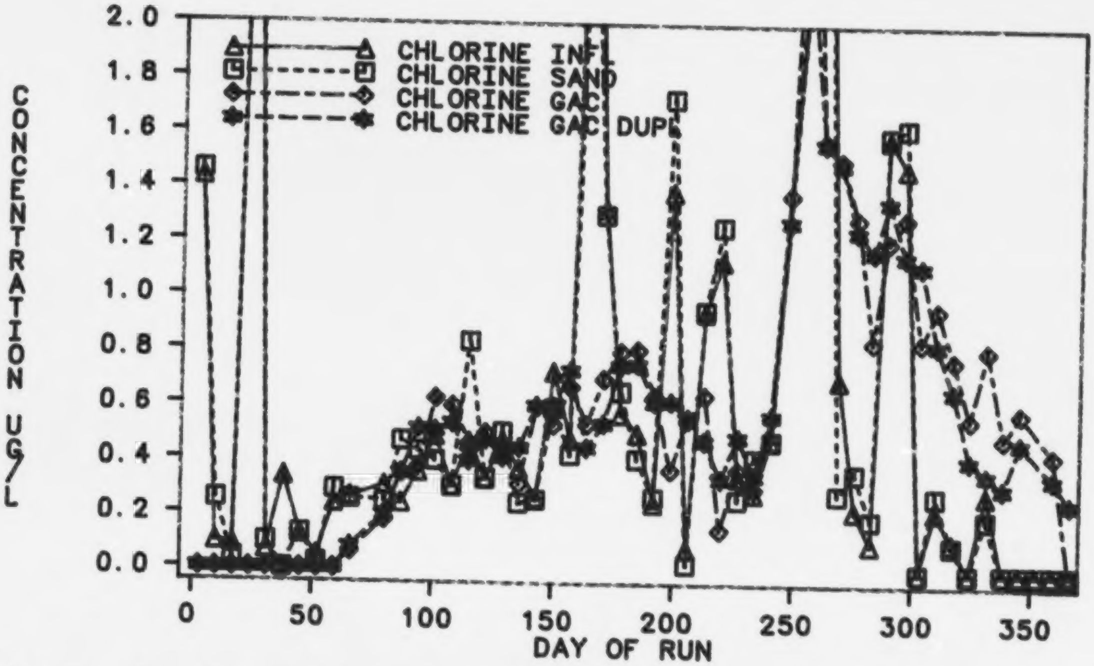


Figure 68. 1,2-dichloroethane Breakthrough Profiles for the Nondisinfected and Chlorine Process Streams.

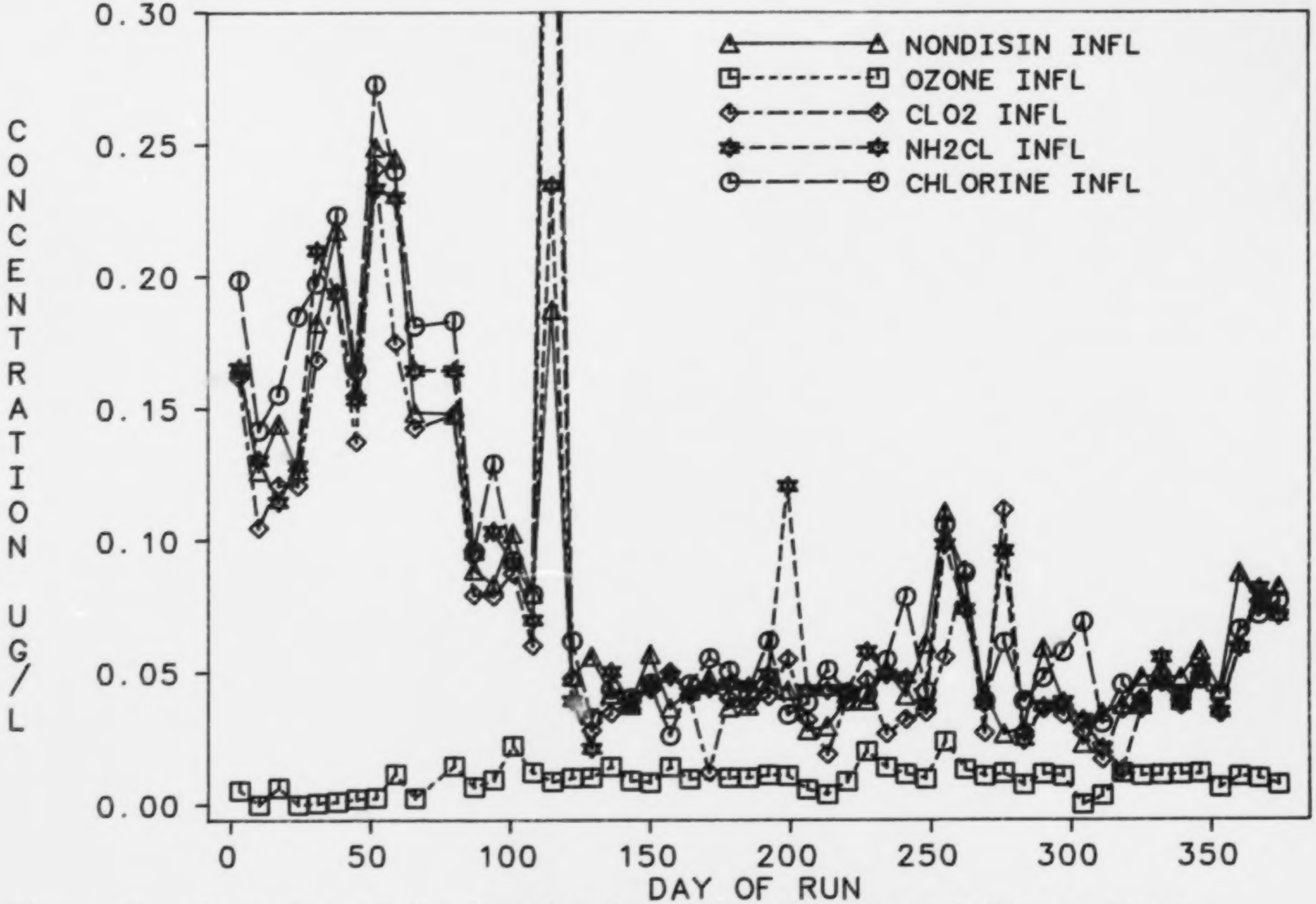


Figure 69. Comparison of the Atrazine Influent Levels for each Process Stream.

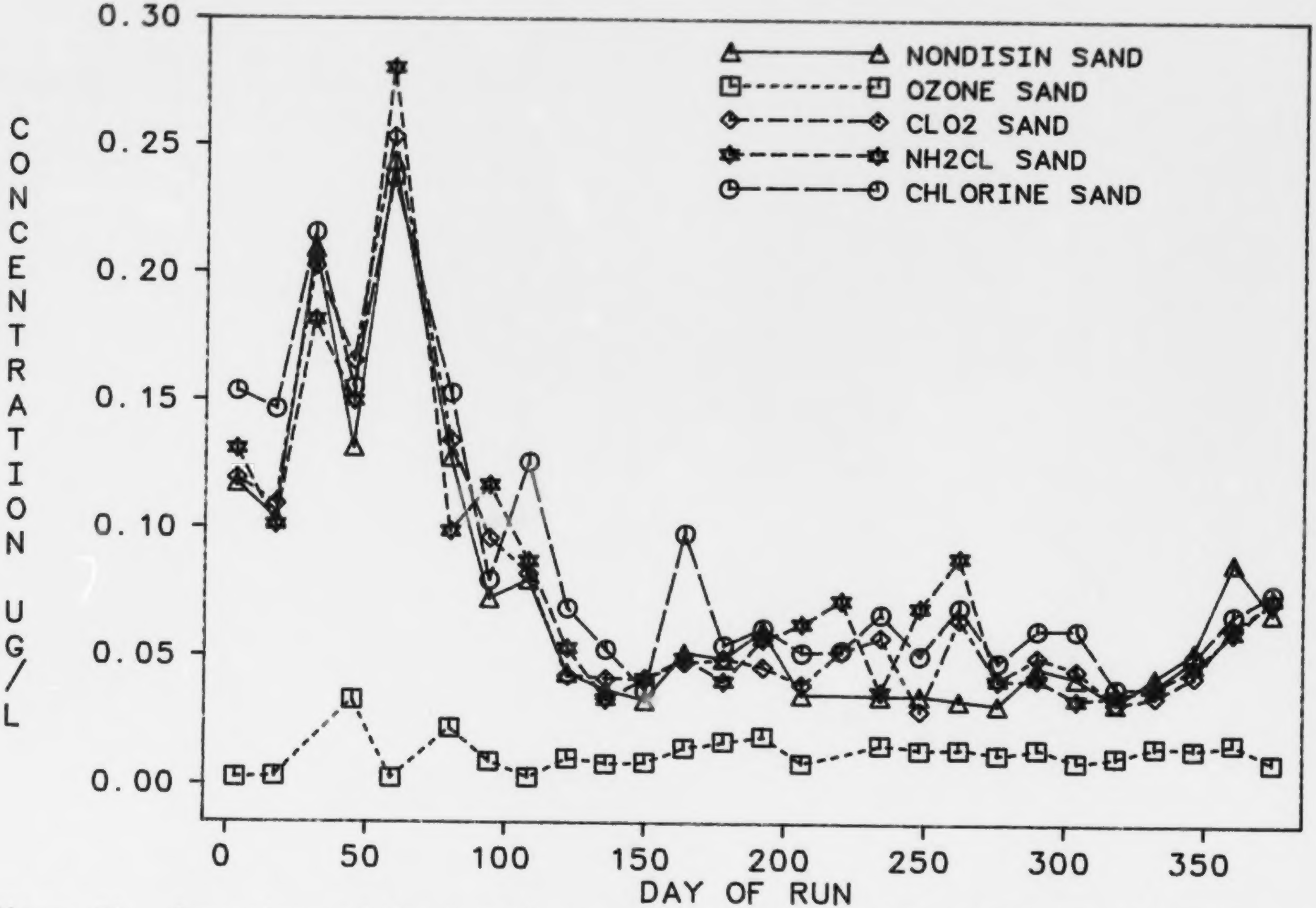


Figure 70. Comparison of the Atrazine Sand Effluent Levels for each Process Stream.

reductions observed across any of the sand columns. The lower concentrations observed for the ozone sand column were produced by ozonation as indicated in Figure 71 which depicts the change in atrazine levels across the ozone process stream.

A comparison of the atrazine effluent concentrations of the GAC and GAC duplicate columns of each process stream is presented in Figure 72. The effluent concentrations as well as the average removals relative to the nondisinfected influent for all of the GAC and GAC duplicate columns were essentially the same. However, those for the nondisinfected process stream were slightly lower at 90 and 94% than those of the other process streams which ranged from 95-97%. The removal of atrazine through GAC filtration was relatively continuous across the operational period in that no breakthrough was evident as indicated in Figure 73 which compares the atrazine levels observed throughout the nondisinfected process stream. These levels are typical of those of all of the process streams except for those of the ozone process stream previously presented in Figure 71. Thus, these data indicate that 30 minutes of disinfectant contact time with those disinfectants used in this study had virtually no effect on the removal of atrazine via GAC filtration with an average EBCT of 20 minutes over a one year operational period.

ALACHLOR

The alachlor levels observed in the nondisinfected influent of the pilot column system ranged from 13-593 ng/l over the operational period with an average of 127 ng/l. These influent levels are compared to those of the disinfected process streams in Figure 74. As with atrazine, alachlor was also uneffected by chlorine dioxide, chloramine, and free chlorine but was reduced an average of 84% by ozonation. There were no reductions observed across any of the sand columns as indicated in Figure 75. The lower levels observed for the ozone sand column were due to ozonation as indicated in Figure 76 which shows that the ozone influent levels were essentially the same as the ozone sand column effluent levels.

A comparison of the effluent alachlor levels observed for the GAC and GAC duplicate columns of each process stream are presented in Figure 77. The effluent concentrations for all of the GAC and GAC duplicate columns were essentially identical up to day 200 at which point the effluent concentration of the nondisinfected GAC column increased slightly resulting in an average removal of 91%. This increase was not observed for the nondisinfected GAC duplicate column whose average removal was 94% which compares closely with the 94-97% removals observed for the disinfected GAC and GAC duplicate columns. As was the case for

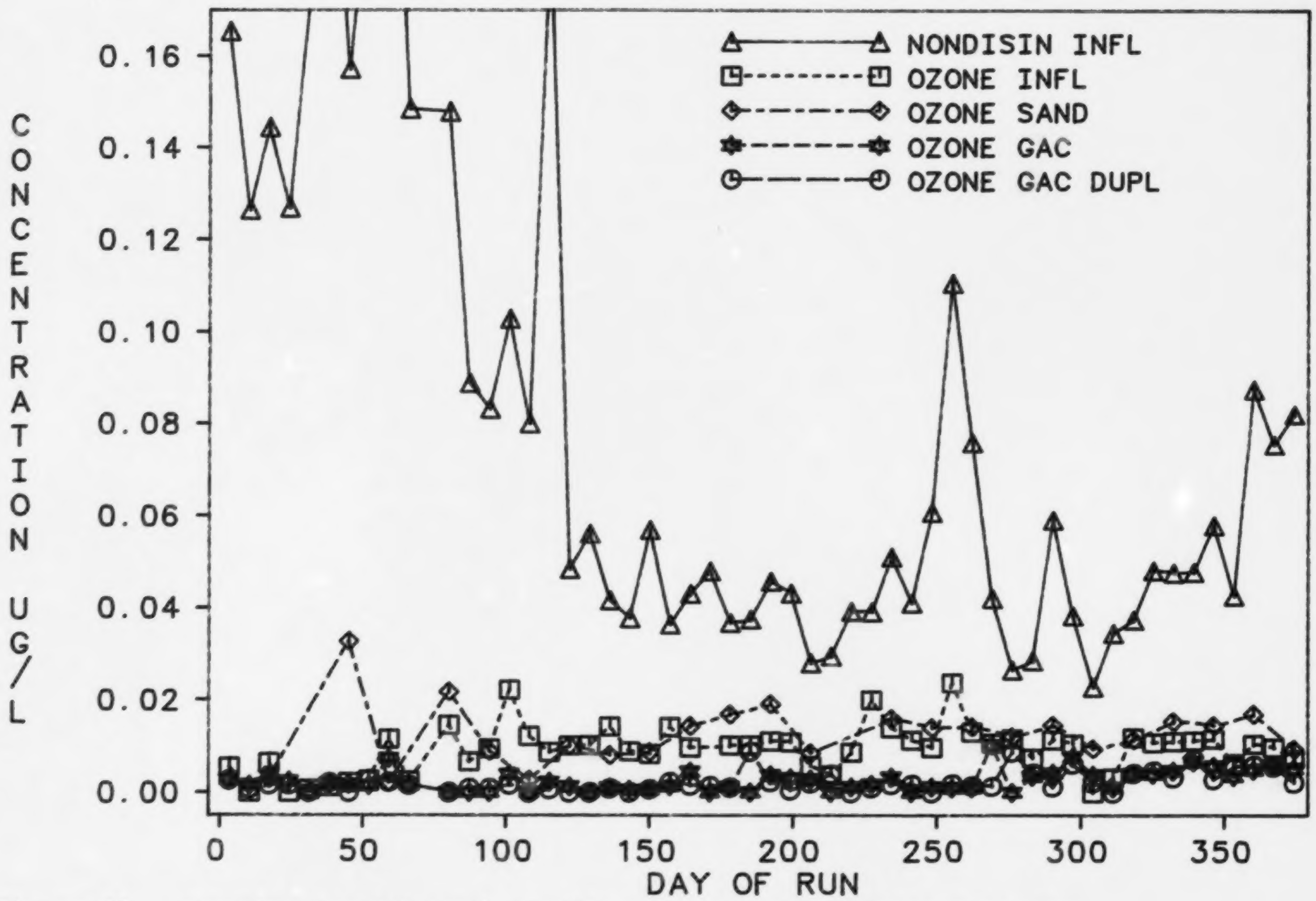
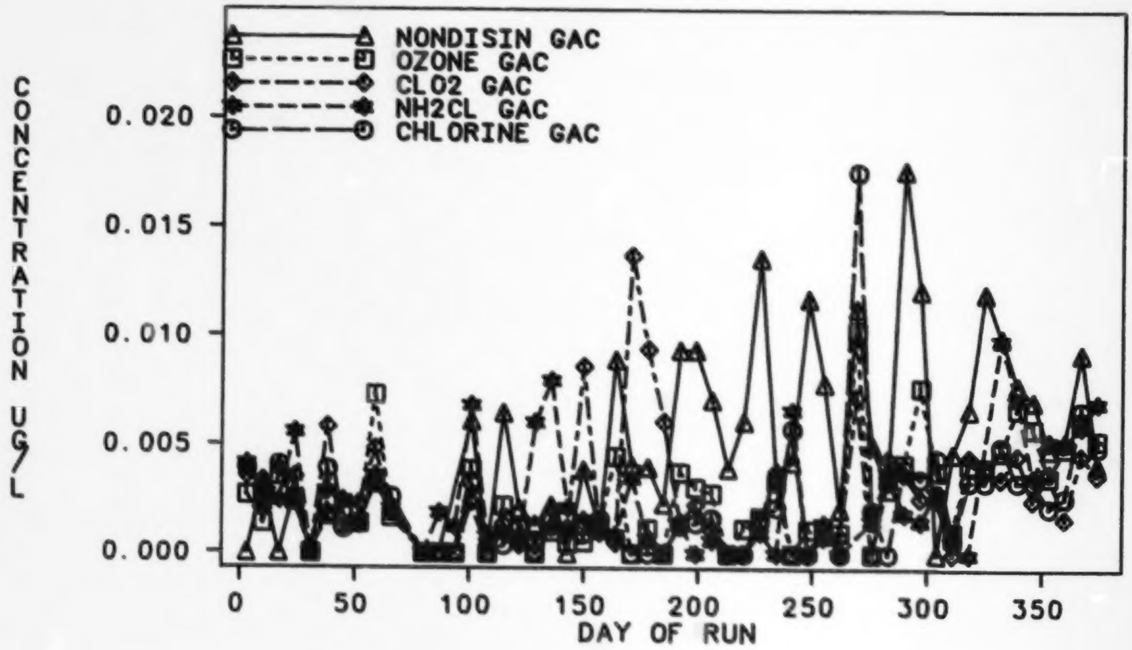


Figure 71. Atrazine Breakthrough Profiles for the Ozone Process Stream.



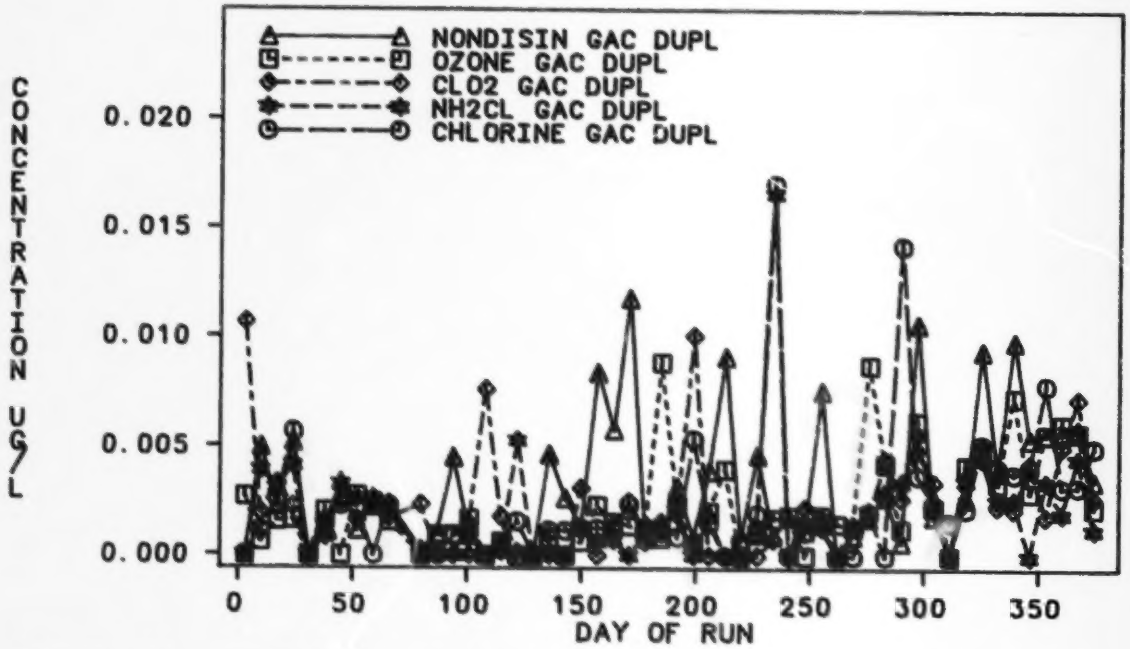


Figure 72. Comparison of the Atrazine GAC and GAC Duplicate Effluent Levels for each Process Stream.

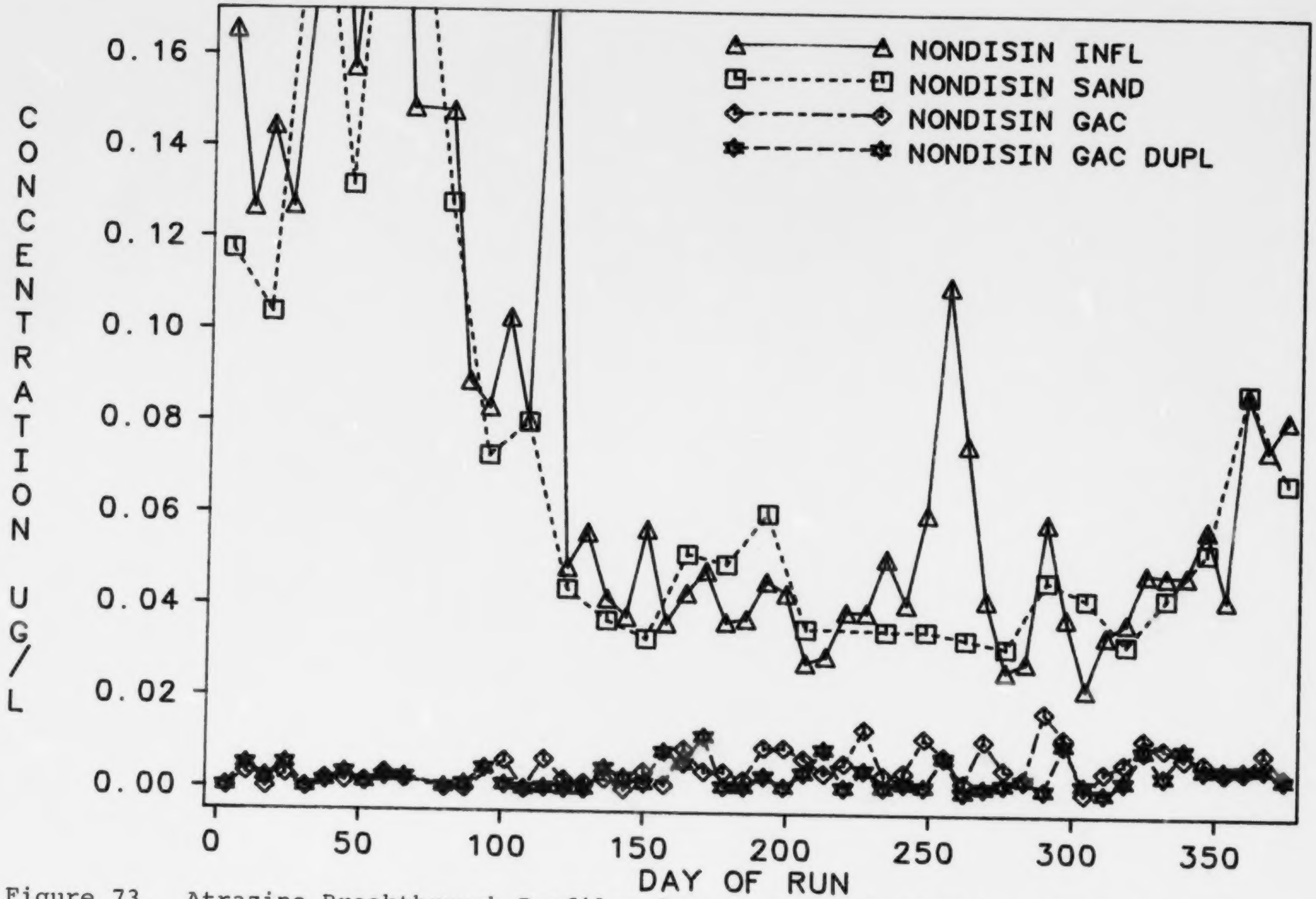


Figure 73. Atrazine Breakthrough Profiles for the Nondisinfected Process Stream.

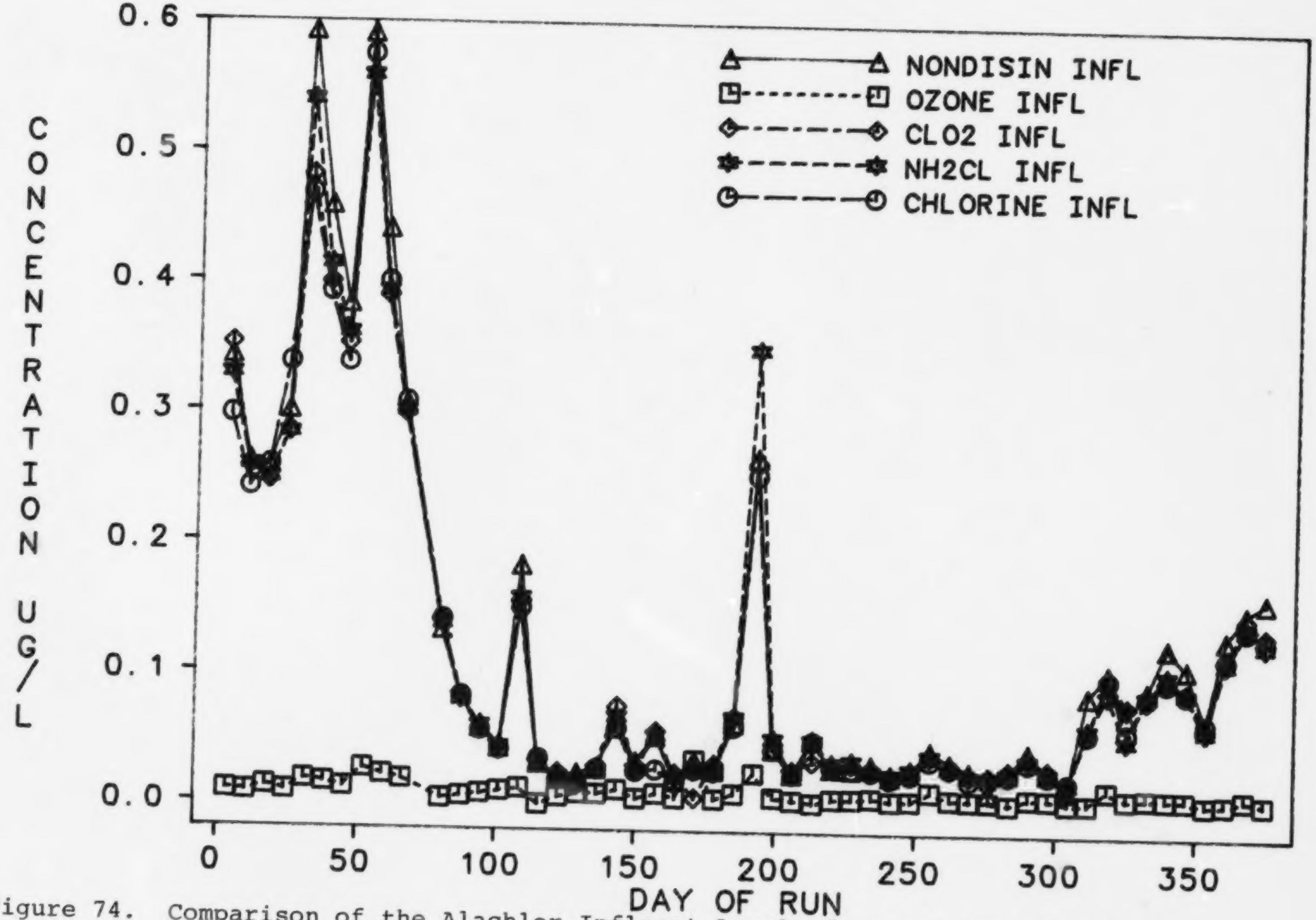


Figure 74. Comparison of the Alachlor Influent Levels for each Process Stream.

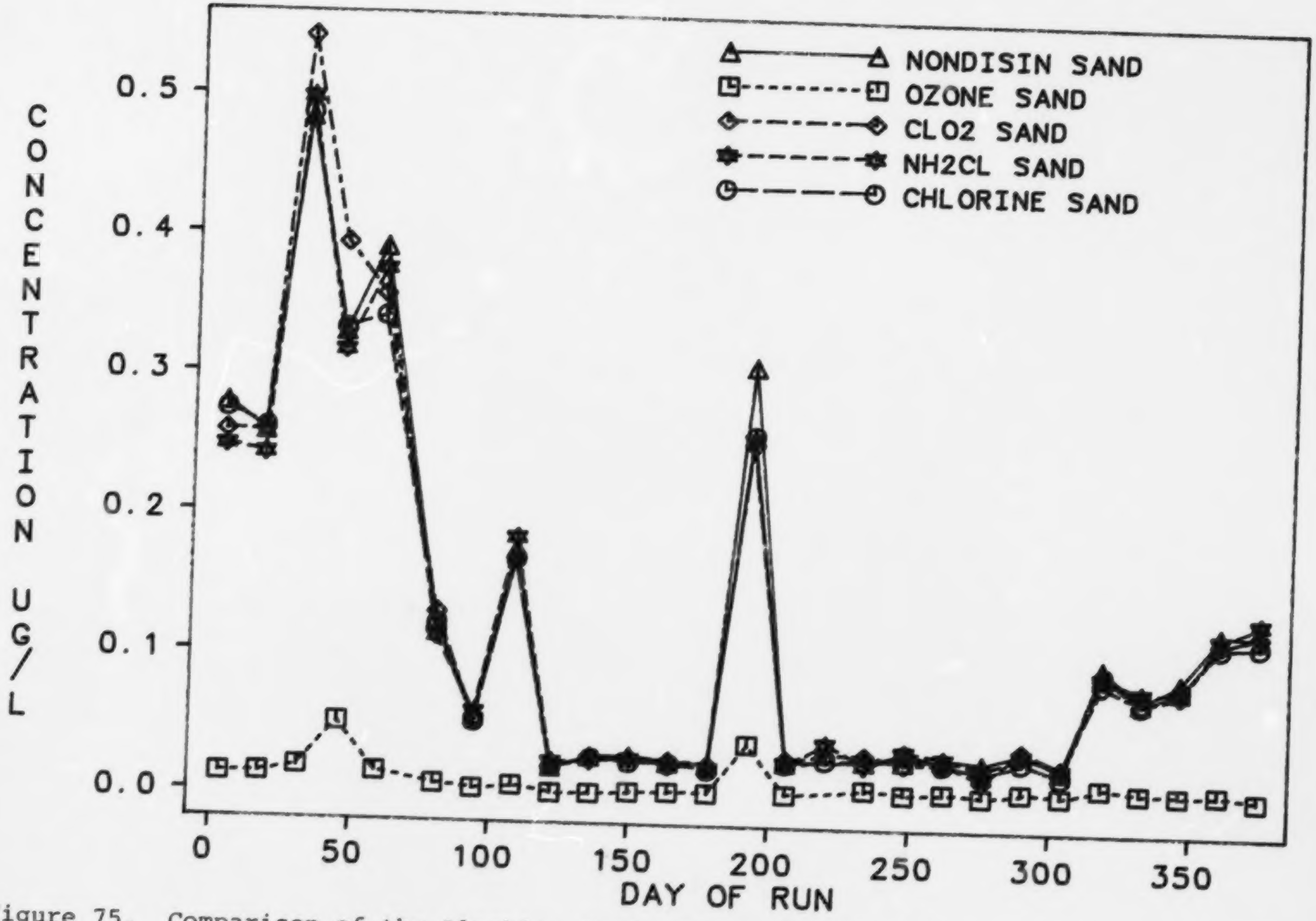


Figure 75. Comparison of the Alachlor Sand Effluent Levels for each Process Stream.

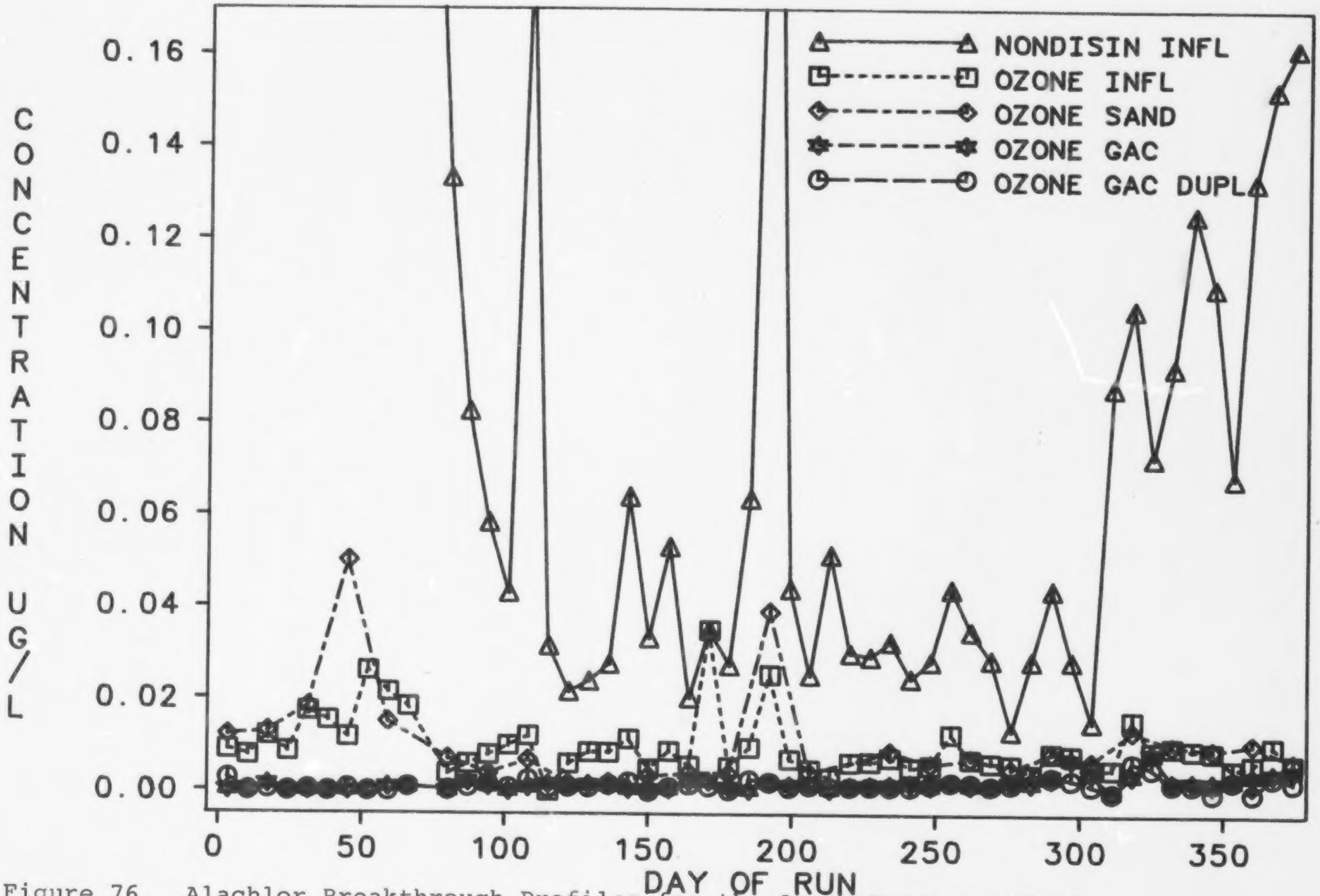
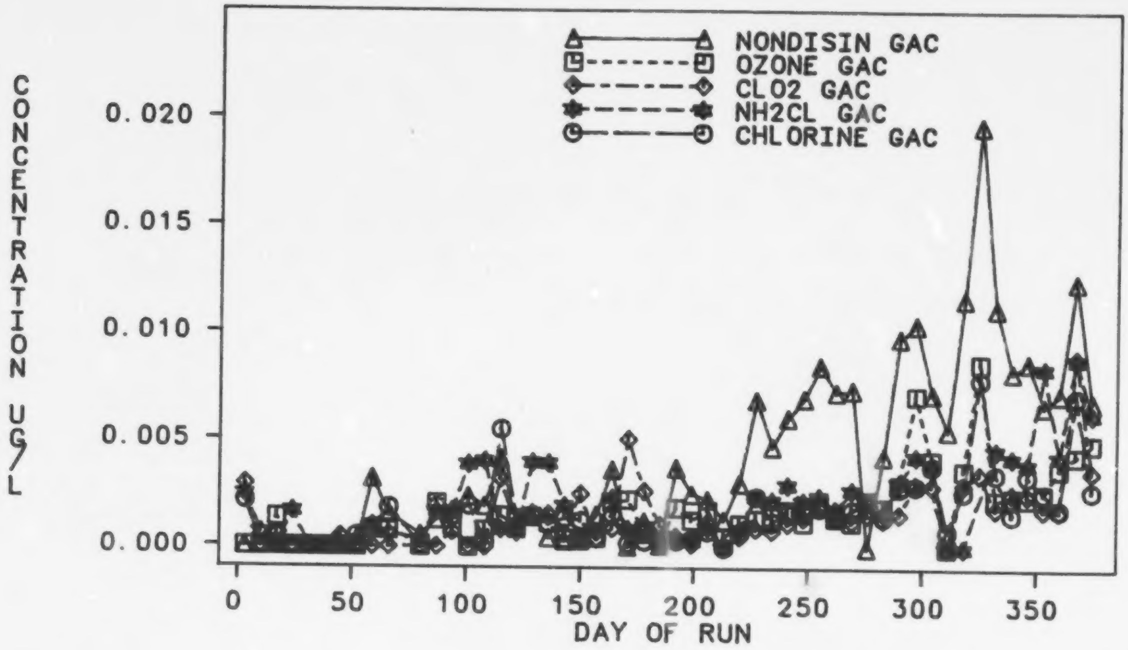


Figure 76. Alachlor Breakthrough Profiles for the Ozone Process Stream.



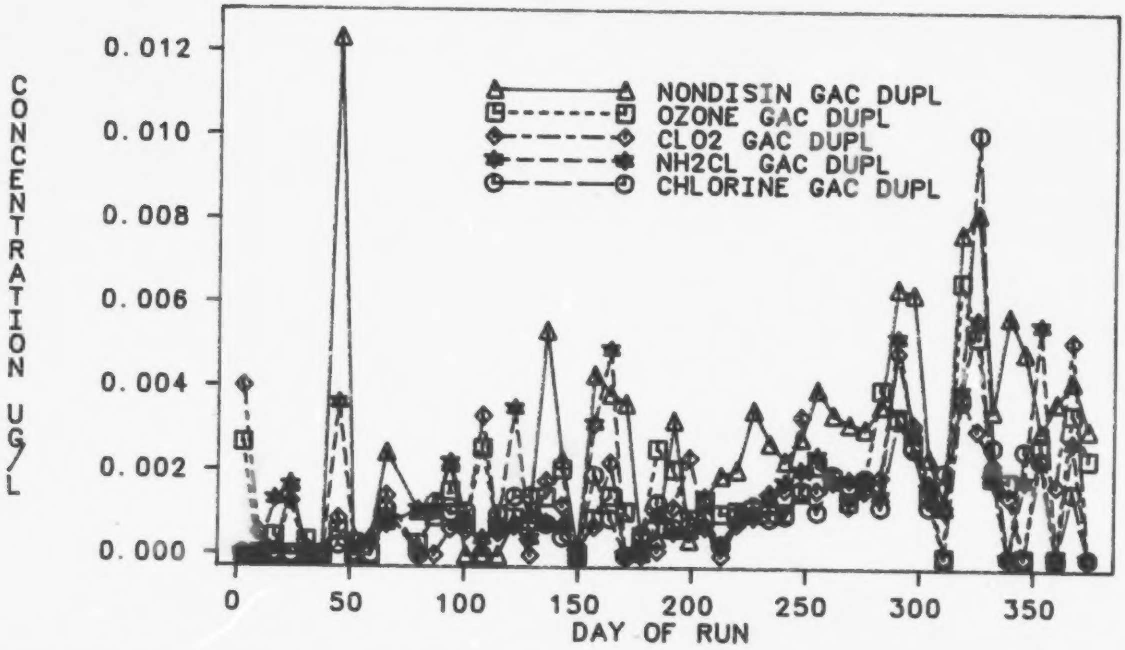


Figure 77. Comparison of the Alachlor GAC and GAC Duplicate Effluent Levels for each Process Stream.

atrazine, these data indicate that 30 minutes of disinfectant contact time had virtually no effect upon the removal of alachlor through GAC filtration with an average EBCT of 20 minutes over a one year operational period. The removal of alachlor across the operational period was rather uniform as typified by the chloramine process stream in Figure 78 with no evidence of breakthrough.

TOTAL CHLORINATED HYDROCARBON INSECTICIDE (CHI)

Total chlorinated hydrocarbon insecticide (CHI) is the summation of all of the individual CHI's monitored during the operational period whose nondisinfected influent concentration averaged less than 10 ng/l. These substances are listed in Table 24 along with their frequency of occurrence and the minimum, maximum, and average concentrations at which they were detected. This list excludes both atrazine and alachlor, which have been previously discussed, due to their considerably higher concentrations which would have masked any effect of those CHI's occurring at lower concentrations. It should be noted that a summation of the individual values indicated in Table 24 would not represent the actual minimum, average, and maximum Total CHI concentrations present since the various individual constituents comprising Total CHI minimized and maximized at different times.

The total CHI concentration in the nondisinfected influent of the pilot column system ranged from 18-88 ng/l with an annual average of 36 ng/l. As indicated in Figure 79, these substances were essentially unaffected by all of the disinfectants used in this study except for ozone which produced an average total CHI reduction of 57%. A comparison of the total CHI levels in the effluents of the sand columns in Figure 80 indicates that there was essentially no removal attributable to sand filtration since the lower concentrations observed for the ozone sand column were essentially identical to those of the ozone influent as indicated in Figure 81. A comparison of the total CHI levels in the combined effluents of the GAC and GAC duplicate columns in Figure 82 shows that the effluent concentrations and hence the removals for all of the GAC columns were essentially the same ranging from 90-93% thus indicating that disinfection prior to GAC filtration had little effect upon the removal of total CHI by GAC filtration with a 20 minute EBCT over a one year operational period. A typical profile of GAC removal for all of the process streams except for the ozone system is presented in Figure 83 for the chlorine dioxide process stream. As with atrazine and alachlor, no breakthrough was evident across the operational period.

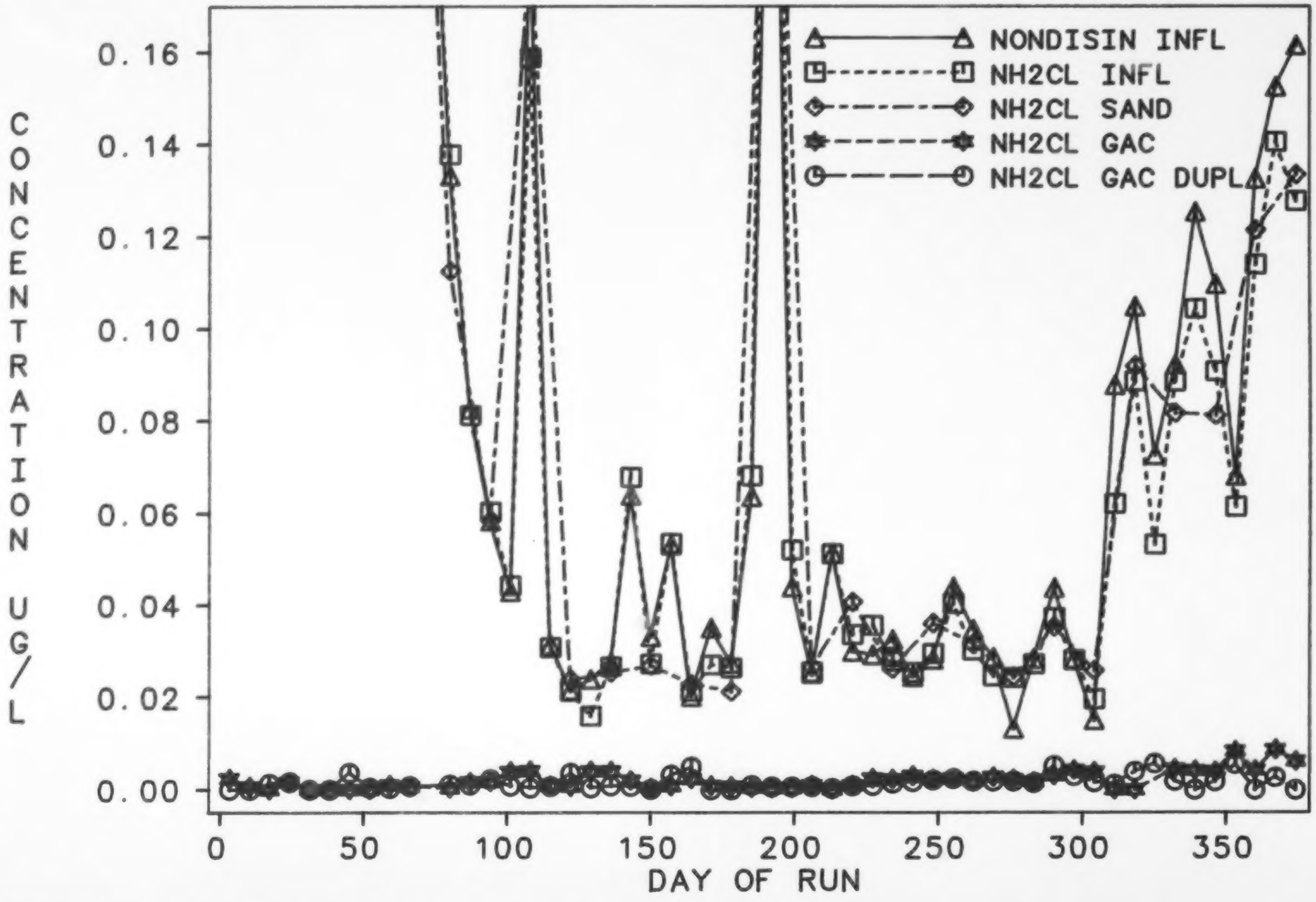


Figure 78. Alachlor Breakthrough Profiles for the Chloramine Process Stream.

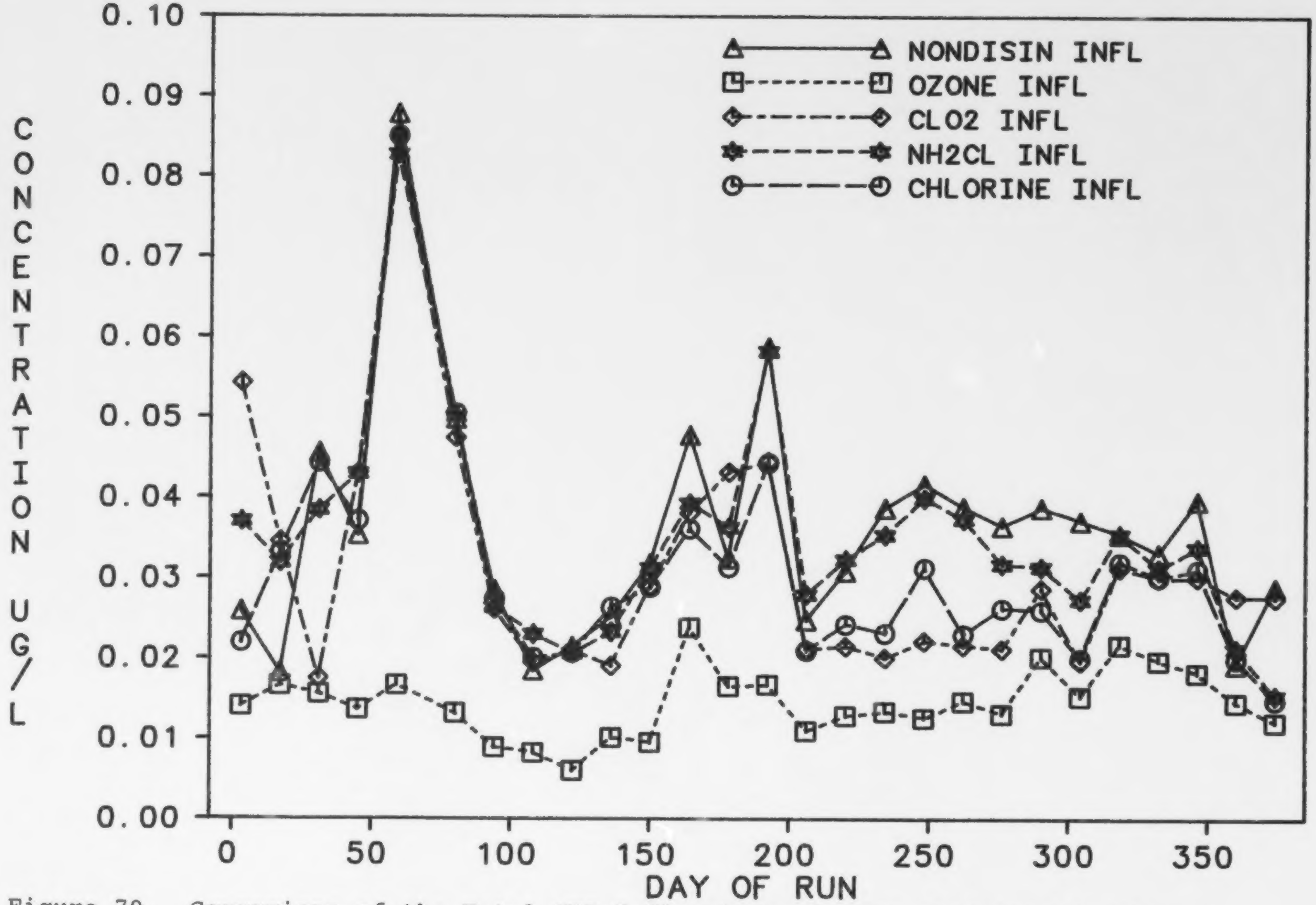


Figure 79. Comparison of the Total CHI Influent Levels for each Process Stream.

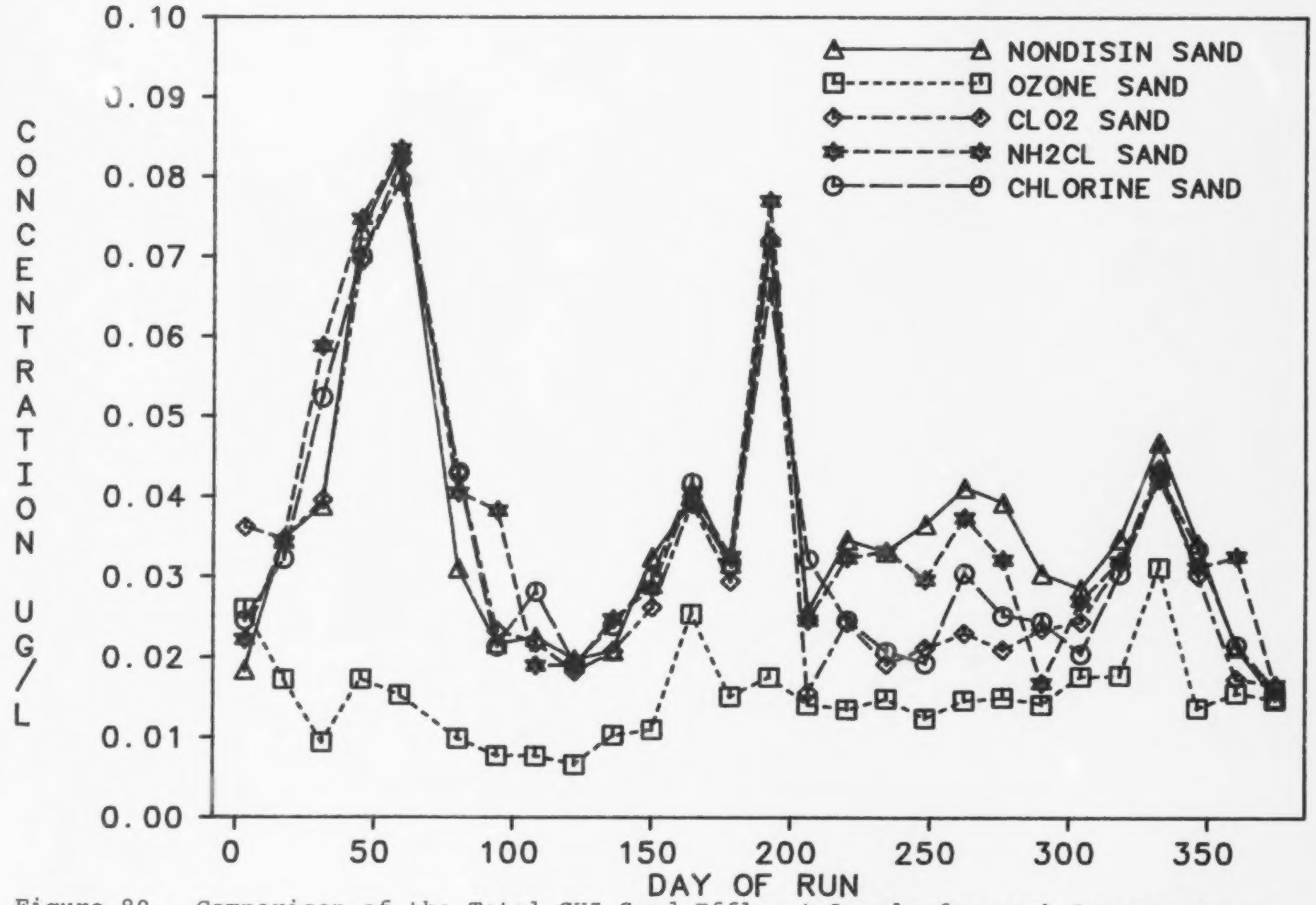


Figure 80. Comparison of the Total CHI Sand Effluent Levels for each Process Stream.

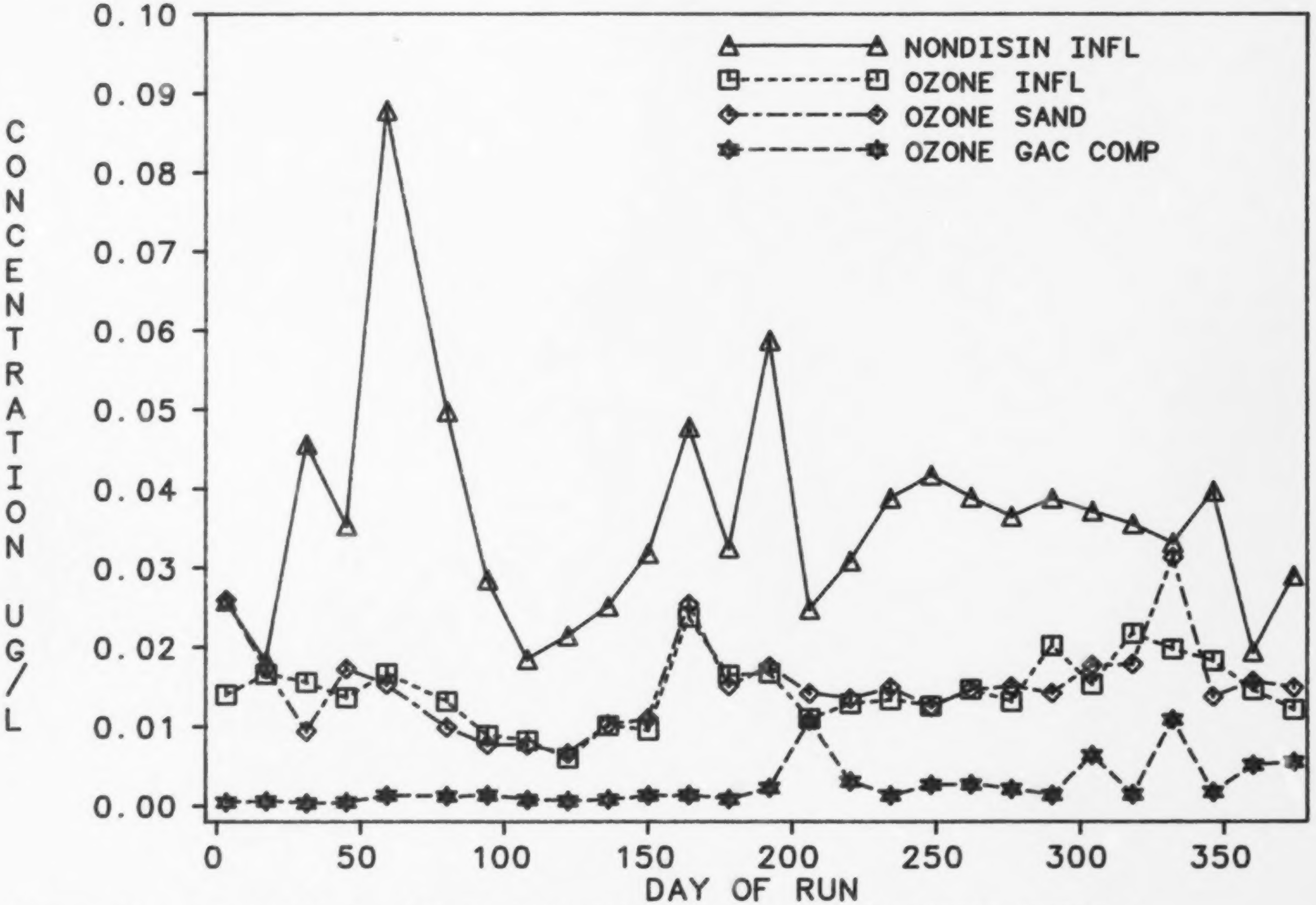


Figure 81. Total CHI Breakthrough Profiles for the Ozone Process Stream.

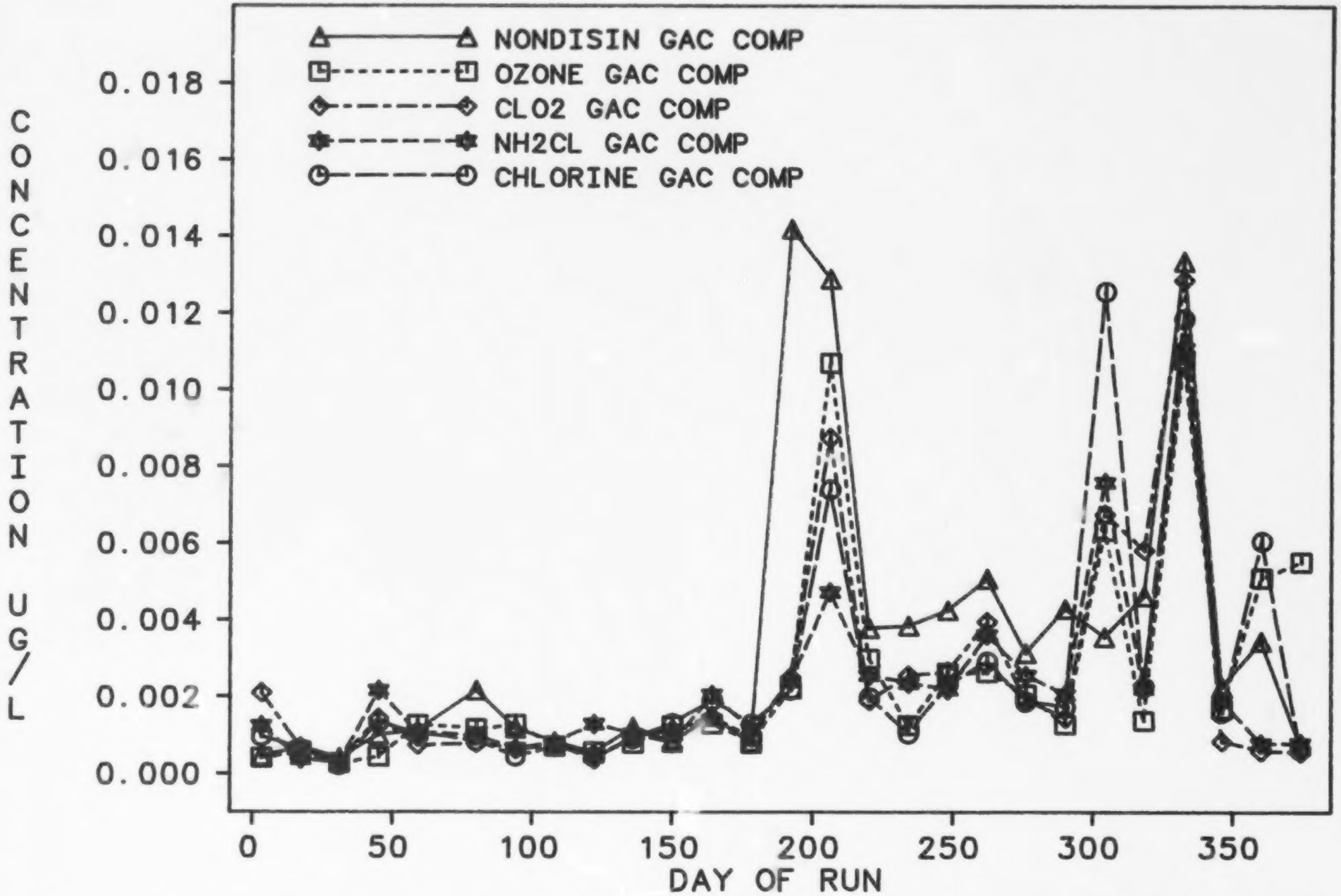


Figure 82. Comparison of the Total CHI Combined GAC Effluent Levels for each Process Stream.

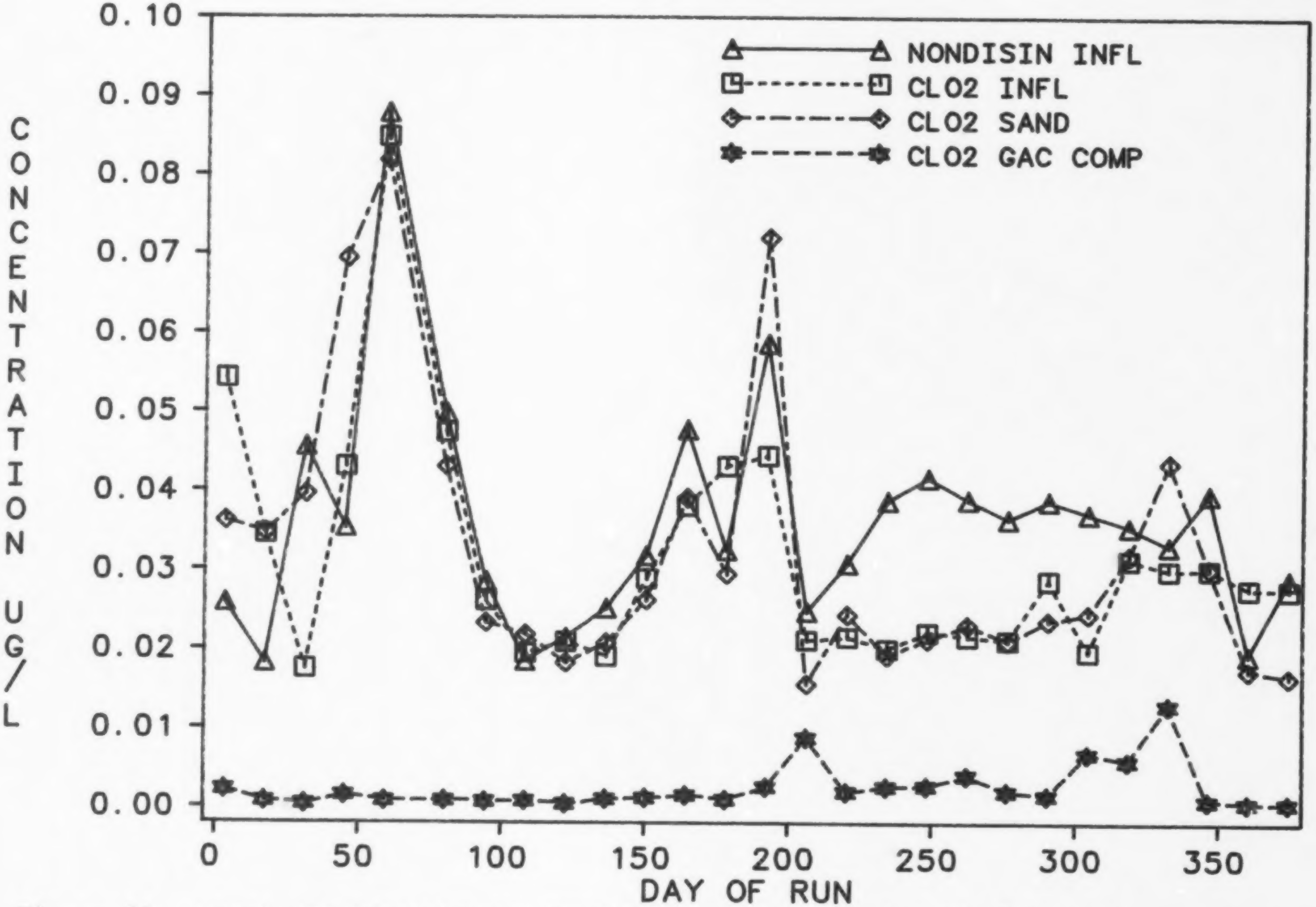


Figure 83. Total CHI Breakthrough Profiles for the Chlorine Dioxide Process Stream.

TABLE 24: FREQUENCY OF OCCURRENCE AND CONCENTRATION RANGES IN THE NONDISINFECTED INFLUENT OF CHLORINATED HYDROCARBON INSECTICIDES COMPRISING TOTAL CHI

		DETECTED CONC. (NG/L)		
CHI	FREQUENCY (%)	MIN.	AVE	MAX
aldrin	100	0.20	0.53	0.92
α-BHC	100	1.14	2.78	6.75
β-BHC	100	0.87	1.64	3.33
γ-BHC	100	0.40	1.39	9.06
α-chlordane	100	0.12	0.27	0.47
γ-chlordane	100	0.15	0.31	0.55
oxy-chlordane	92	0.02	0.09	0.35
α-chlordene	89	0.02	0.14	0.46
β-chlordene	93	0.08	7.55	32.5
γ-chlordene	95	0.05	0.43	0.77
DCPA*	100	0.17	1.42	5.42
o,p'-DDD	100	0.13	0.44	1.13
m,p'-DDD	56	0.03	0.36	1.34
p,p'-DDD	93	0.17	0.57	1.28
o,p'-DDE	96	0.08	0.30	0.83
p,p'-DDE	100	0.06	0.15	0.32
o,p'-DDT	59	0.03	0.68	7.80
p,p'-DDT	85	0.07	0.36	1.25
dieldrin	100	1.63	2.84	5.80
endosulfan-2	96	0.02	0.29	0.72
endrin	100	0.25	0.67	1.58
heptachlor	92	0.03	6.95	33.3
heptachlor epoxide	100	0.28	0.73	1.68
hexachlorobenzene	100	0.35	0.66	1.59
pentachloronitrobenzene	96	0.04	0.15	0.27
perthane	77	0.85	8.99	23.4

*dimethyl-2,3,5,6-tetrachloroterephthalate

TOTAL ALKYLBENZENE

Total alkylbenzene is a conglomerate of all of the alkylbenzenes monitored during the operational period which are listed in Table 25 along with their frequency of occurrence and the minimum, maximum, and average concentrations at which they were detected. The total alkylbenzene concentration in the nondisinfected influent ranged from 59-10,300 ng/l with an average of 590 ng/l. The concentrations of total alkylbenzene in the influent of each process stream are compared in Figure 84. Excellent removals were observed for ozonation relative to the

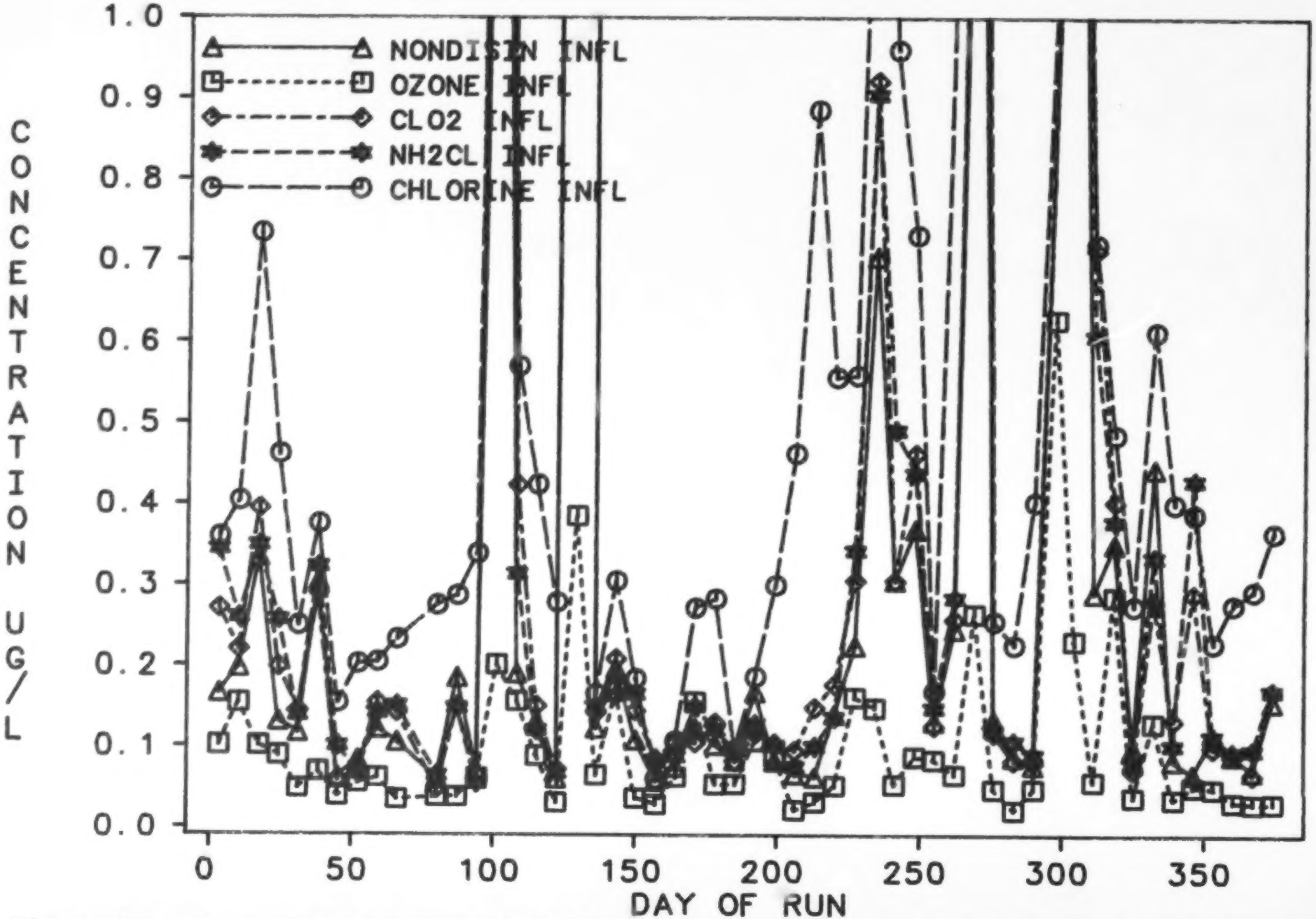


Figure 84. Comparison of the Total Alkylbenzene Influent Levels for each Process Stream.

TABLE 25: FREQUENCY OF OCCURRENCE AND CONCENTRATION RANGES OF ALKYLBENZENES IN THE NONDISINFECTED INFLUENT COMPRISING TOTAL ALKYLBENZES

ALKYLBENZENES	DETECTED FREQUENCY (%)	CONCENTRATION (NG/L)		
		MIN.	AVE.	MAX
cumene	72	0.75	80.4	959
p-cymene	85	0.31	1.70	13.1
1,3-diethylbenzene	92	0.39	2.54	17.0
1,4-diethylbenzene	85	0.27	1.70	11.1
ethylbenzene	75	0.14	121	1985
2-ethyltoluene	100	0.60	4.08	21.5
3-ethyltoluene	89	1.29	9.96	51.0
4-ethyltoluene	85	0.54	10.3	112
1,2,3,4-tetramethylbenzene	98	0.58	3.87	18.2
1,2,3,5-tetramethylbenzene	94	0.98	3.47	15.6
1,2,4,5-tetramethylbenzene	96	0.86	3.49	14.5
1,2,3-trimethylbenzene	100	1.89	6.73	32.5
1,2,4-trimethylbenzene	100	6.19	19.1	91.8
1,3,5-trimethylbenzene	100	1.90	8.24	43.1
o-xylene	98	5.77	120	1912
m & p-xylene*	96	1.18	256	6514

*coeluting peaks

sharp increases observed in the total alkylbenzene concentration while only minimal removals were observed at the lower concentrations for an overall average removal of 52%. Significant increases in total alkylbenzene concentration averaging 11, 14, and 100% were observed for 30 minutes of disinfected contact time with chlorine dioxide, chloramine, and free chlorine, respectively. The formation of alkylbenzenes in the chlorine dioxide and chloramine process streams was attributable to the brief presence of relatively low levels of free chlorine in these process streams. The formation of alkylbenzenes following chlorination will be discussed in greater detail in a later section dealing with disinfection byproducts. The comparison of the total alkylbenzene levels in the effluents of the sand columns in Figure 85 shows that the total alkylbenzene removal of the nondisinfected sand column, which averaged approximately 49%, was equivalent to the reduction observed for ozonation since no further removal was observed across the ozone sand column as indicated in Figure 85. In addition, a 37% average reduction of total alkylbenzene was observed across the chlorine sand column relative to the chlorine

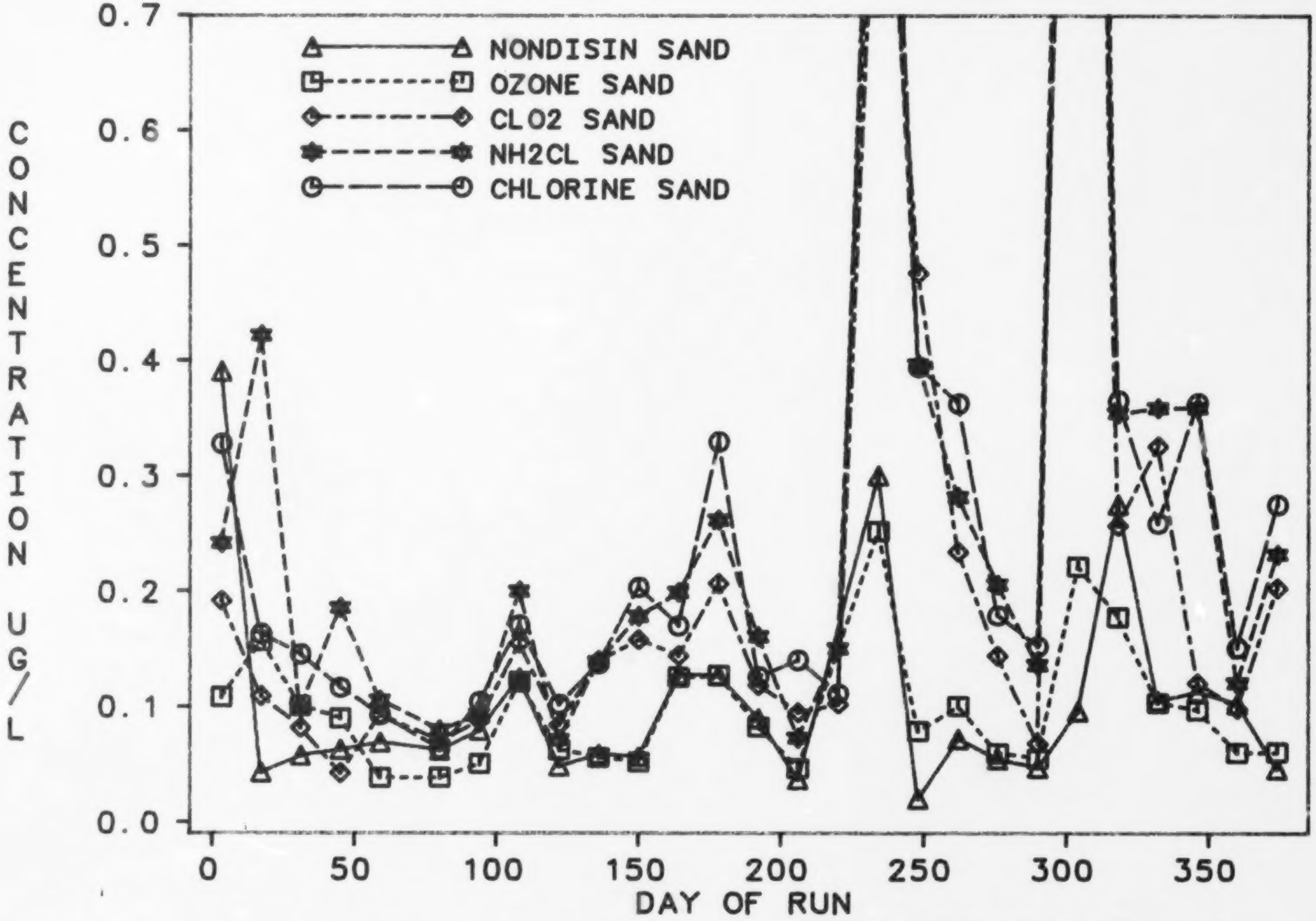


Figure 85. Comparison of the Total Alkylbenzene Sand Effluent Levels for each Process Stream.

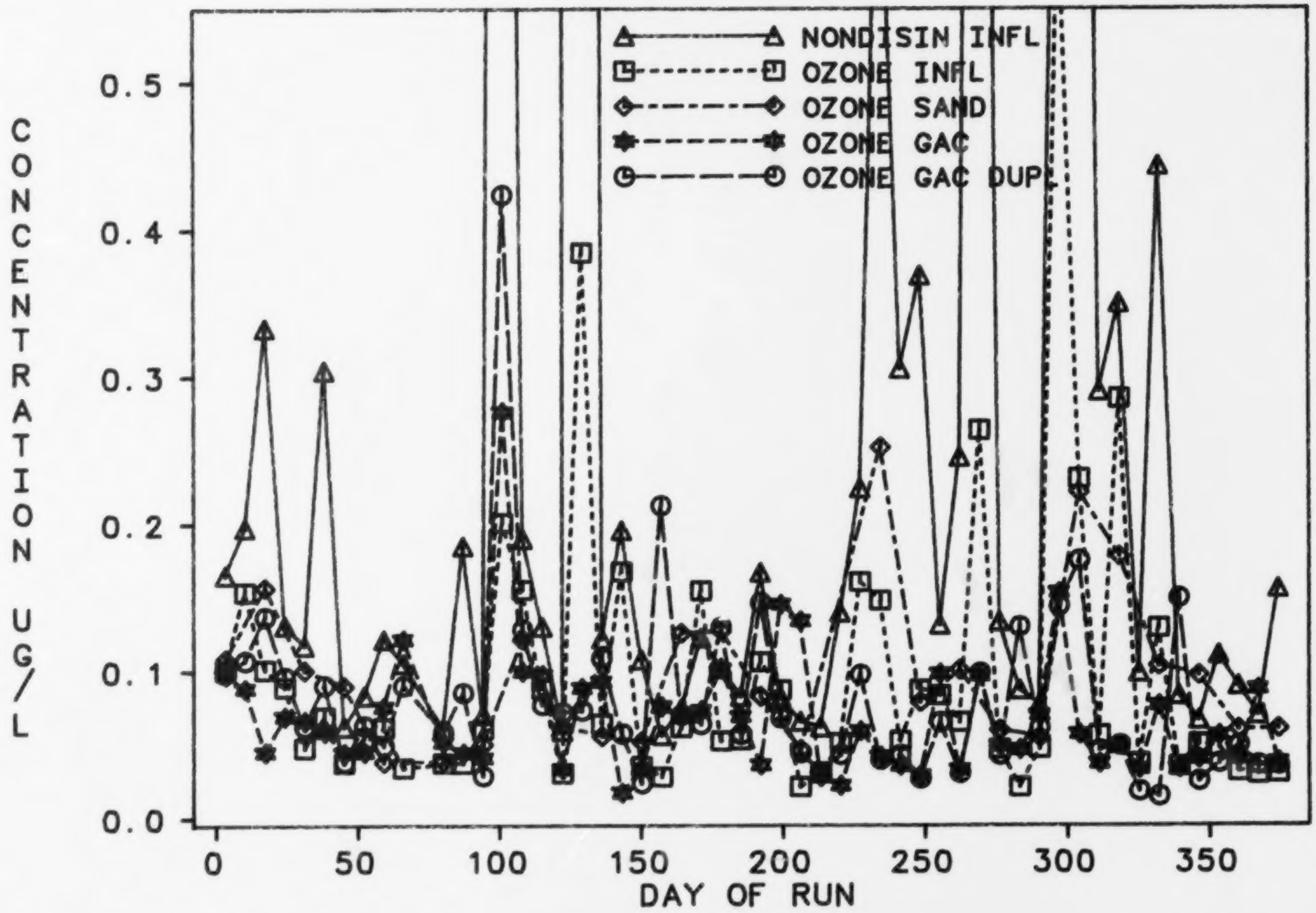
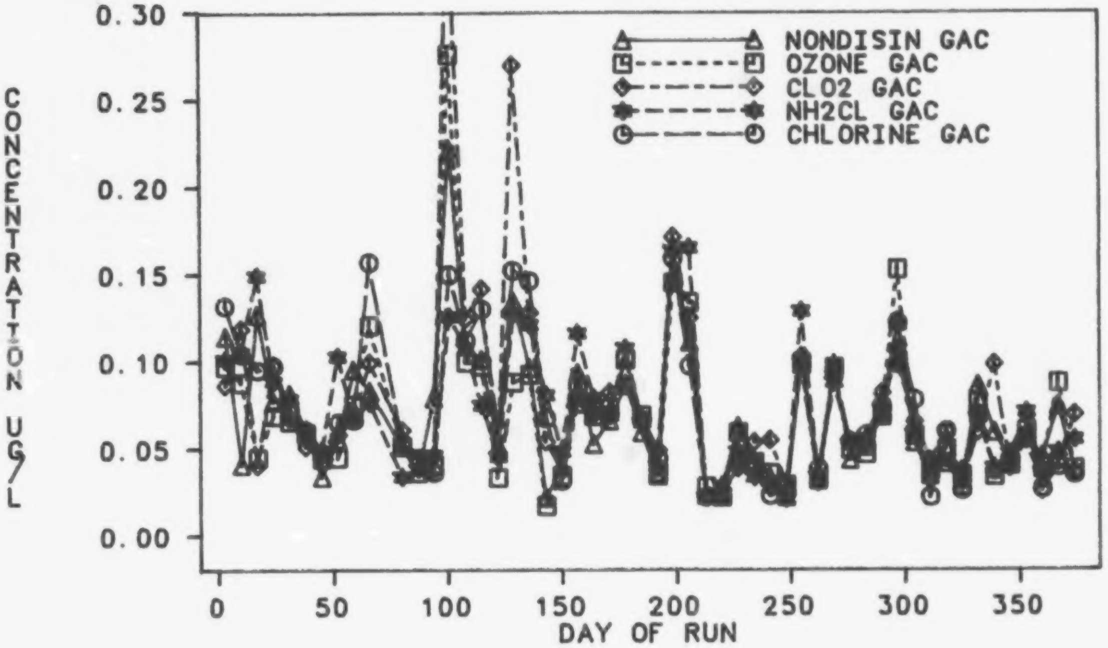


Figure 86. Total Alkylbenzene Breakthrough Profiles for the Ozone Process Stream.

influent. However, the levels in the effluent of this column were, on the average, still 20% greater than that of the nondisinfected influent. The total alkylbenzene levels in the effluents of the GAC and GAC duplicate columns in Figure 87 indicate similiar removals were observed for all process streams. Average removals of 44 and 48% were observed for the nondisinfected GAC and GAC duplicate columns indicating, as depicted in Figure 88, that GAC filtration had essentially no greater effect than sand filtration which averaged approximately 49%. GAC filtration had virtually no effect relative to the removal of alkylbenzenes in the ozone process stream since reductions observed were attributable to ozonation as indicated in Figure 87. Average reductions ranging from 40-45% were observed for the GAC and GAC duplicate columns of the chlorine dioxide and chloramine process streams as indicated in Figure 89. Average removals of 70 and 76% were observed for the GAC columns of the chlorine process stream with respect to the chlorine influent as indicated in Figure 90. However, the average removals observed for the chlorine GAC columns with respect to the nondisinfected influent of 39 and 46% were similiar to those observed for the other process streams indicating that the loading of alkylbenzenes on the chlorine GAC columns was considerably greater than that of the other GAC columns. There were no standard breakthrough curves observed for any of the GAC columns. In general, GAC filtration was quite ineffective at low concentrations but was considerably better when large increases in total alkylbenzene levels were observed.

TOTAL ALKANE

Total alkane is a summation of all of the normal alkanes listed in Table 26 which contains their frequency of occurrence and the minimum, maximum, and average concentrations at which they were detected. The total alkane concentration in the nondisinfected influent averaged 50 ng/l with a range of 10-150 ng/l. These total alkane levels are compared to those of the disinfected influents in Figure 91. An average removal of 35% was observed for ozonation with greater reductions being observed at the higher nondisinfected influent concentrations which occurred during the latter part of the operational period. No reductions were observed for the other disinfectants. The levels of total alkane in the effluent of the sand columns are compared in Figure 92 and indicate that no significant reductions occurred which could be attributable to sand filtration. The lower concentrations in the ozone sand column effluent were again attributable to ozonation as indicated in Figure 93 in which the influent and effluent levels of the ozone sand column are essentially identical. The total alkane levels in the effluents of the GAC and GAC duplicate columns are compared in Figure 94 which depicts similiar concentrations for all locations



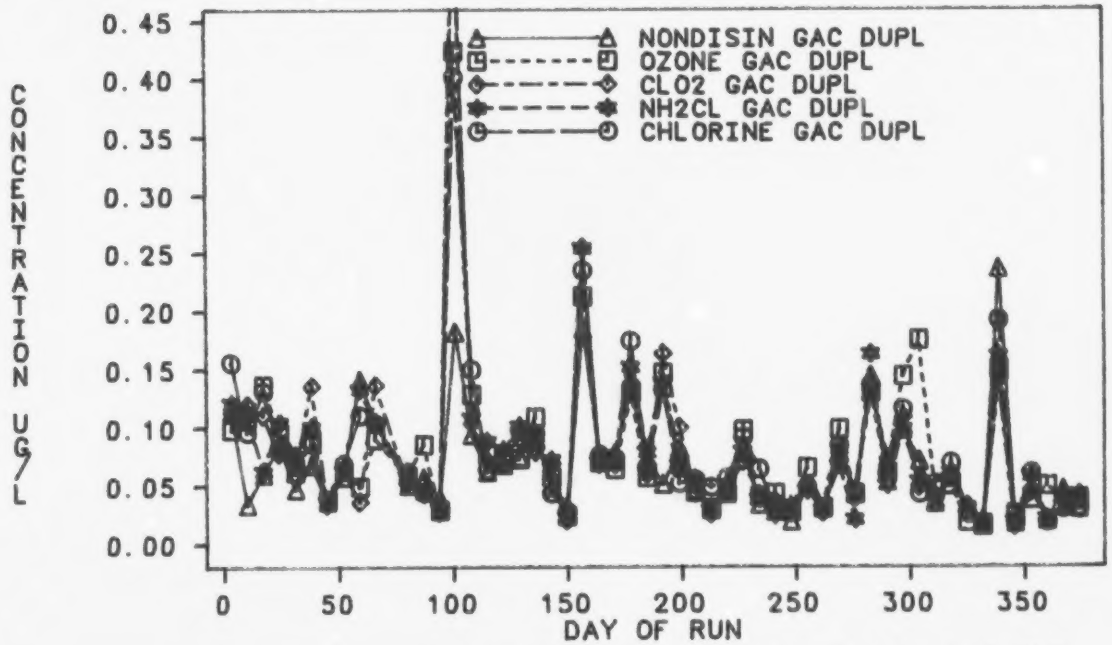


Figure 87. Comparison of the Total Alkylbenzene GAC and GAC Duplicate Effluent Levels for each Process Stream.

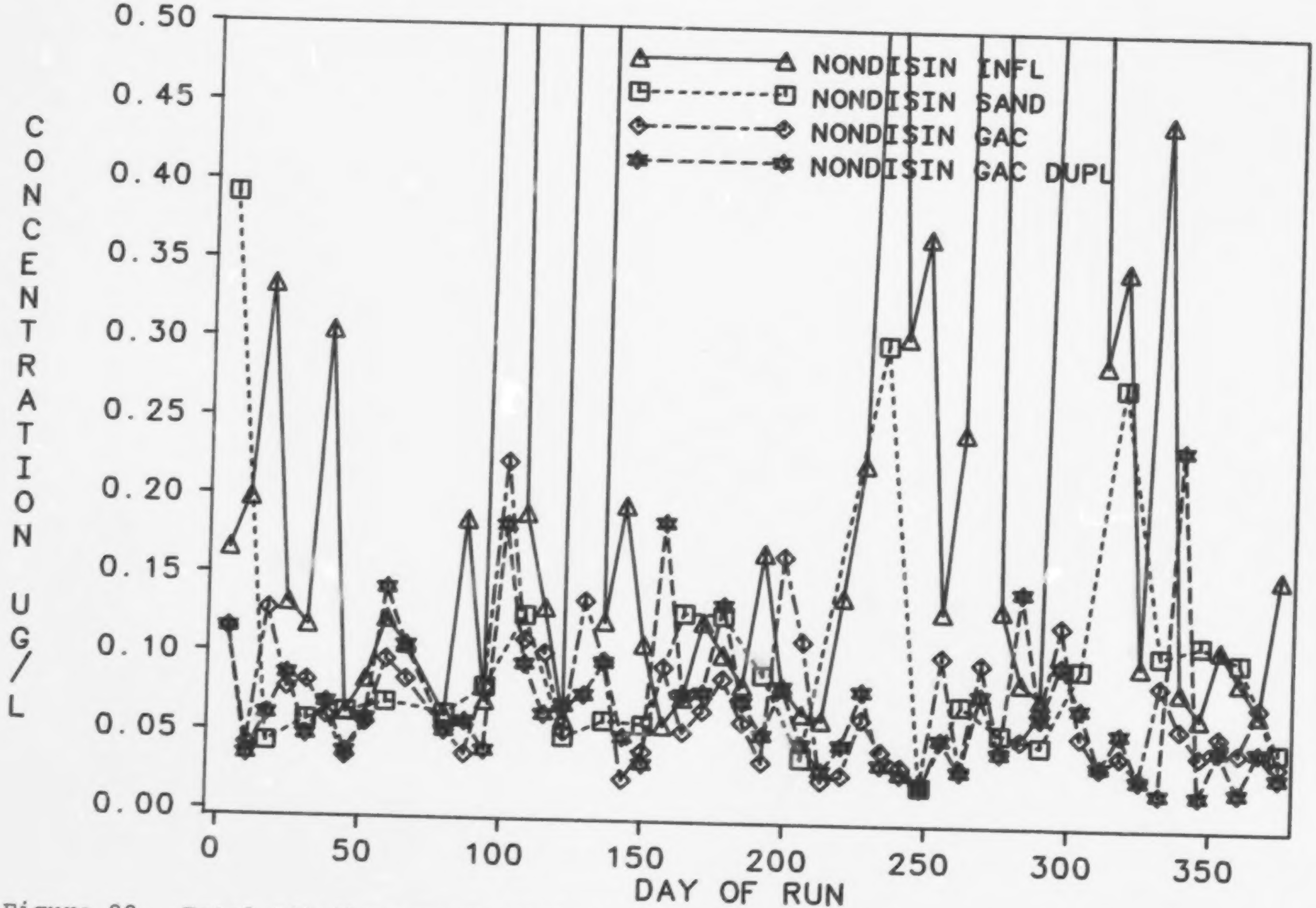


Figure 88. Total Alkylbenzene Breakthrough Profiles for the Nondisinfected Process Stream.

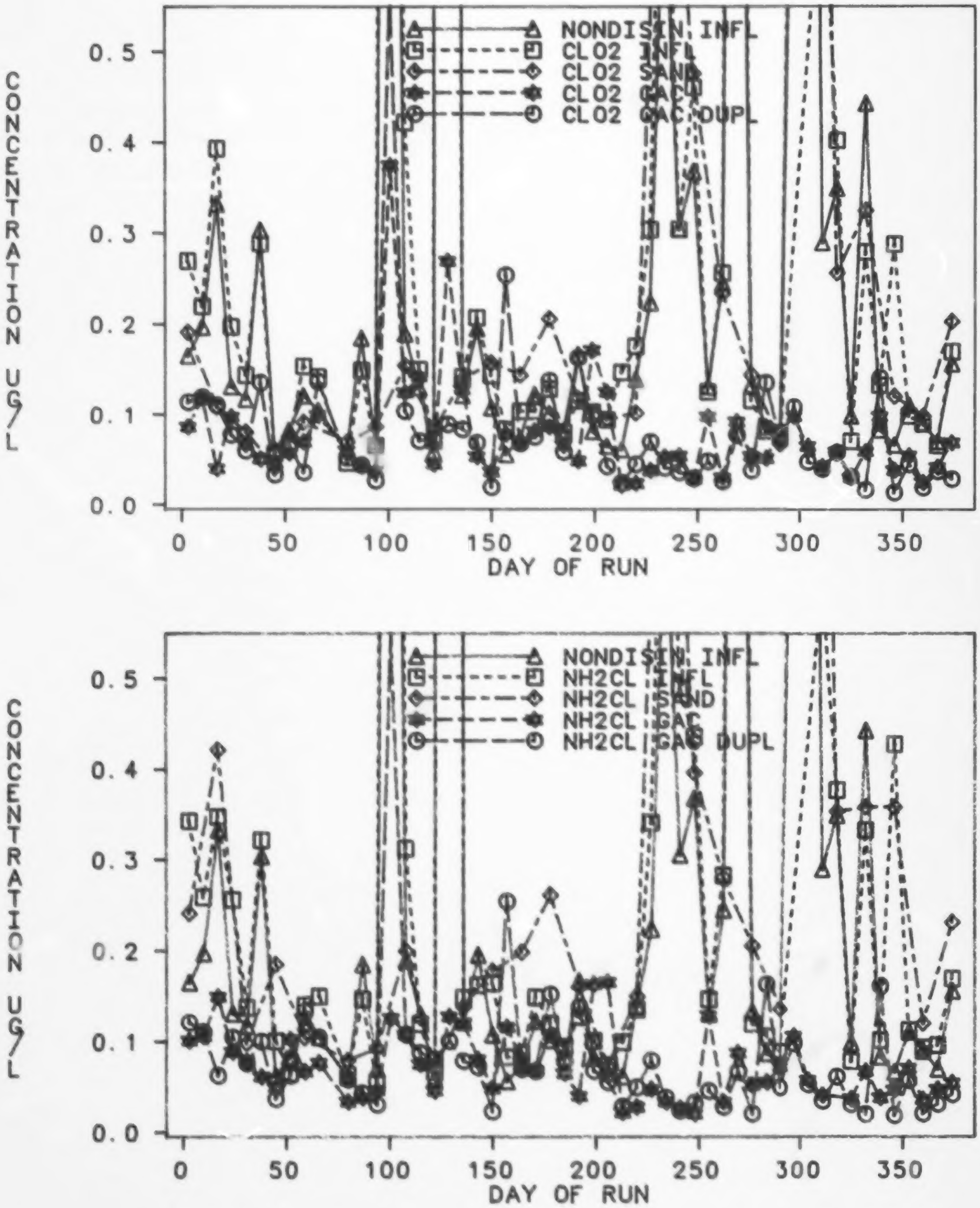


Figure 89. Total Alkylbenzene Breakthrough Profiles for the Chlorine Dioxide and Chloramine Process Streams.

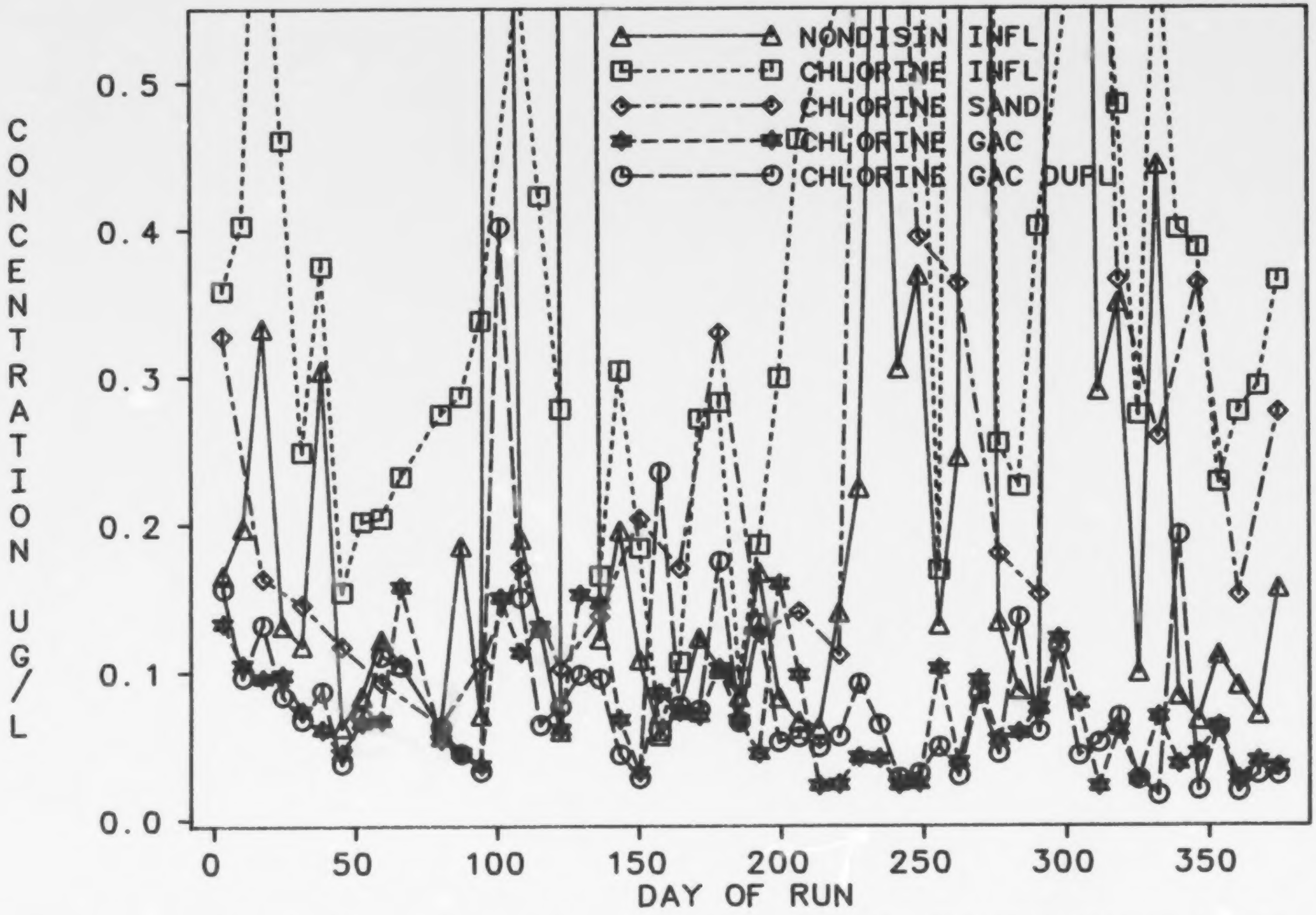


Figure 90. Total Alkylbenzene Breakthrough Profiles for the Chlorine Process Stream.

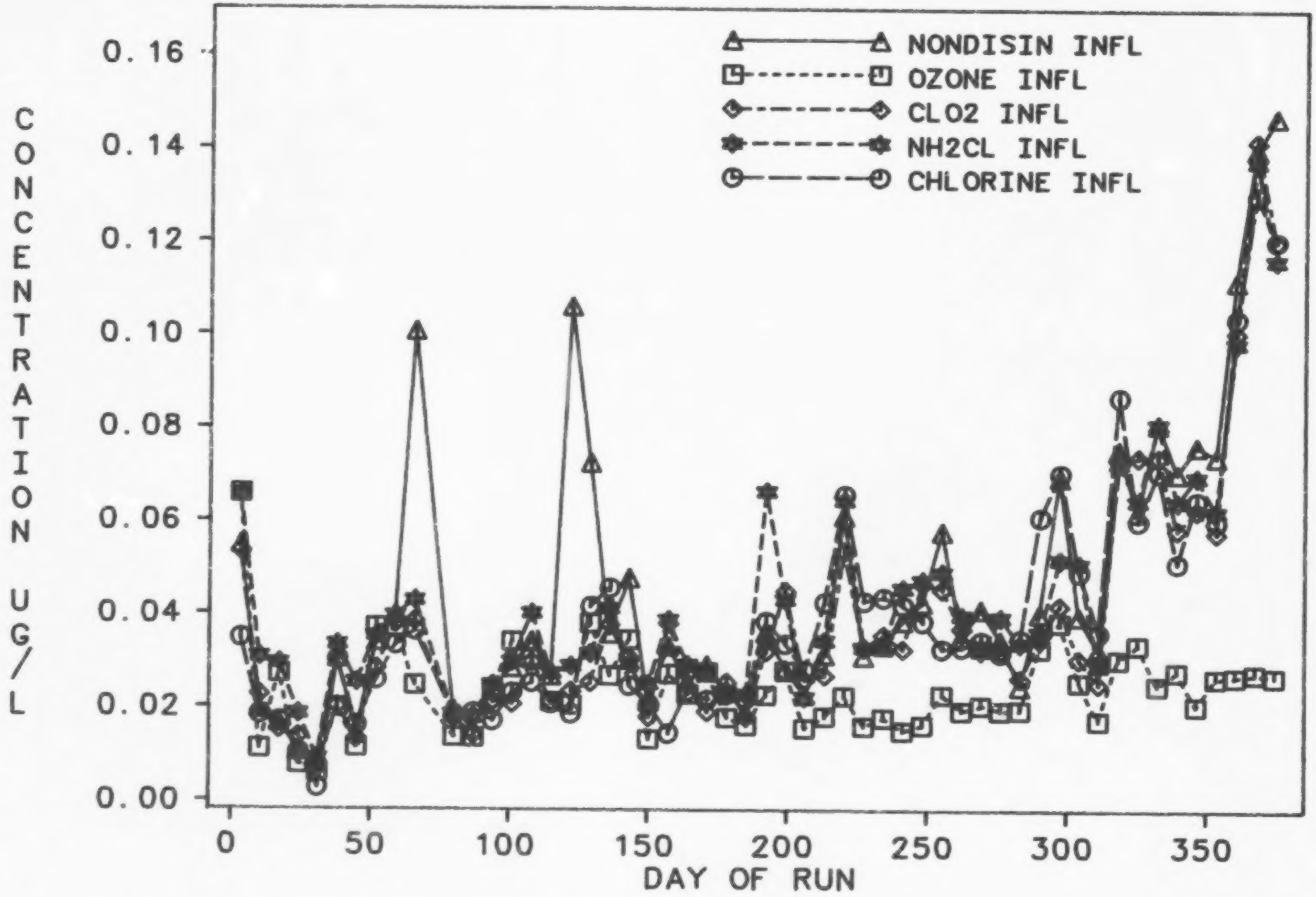


Figure 91. Comparison of the Total Alkane Influent Levels for each Process Stream.

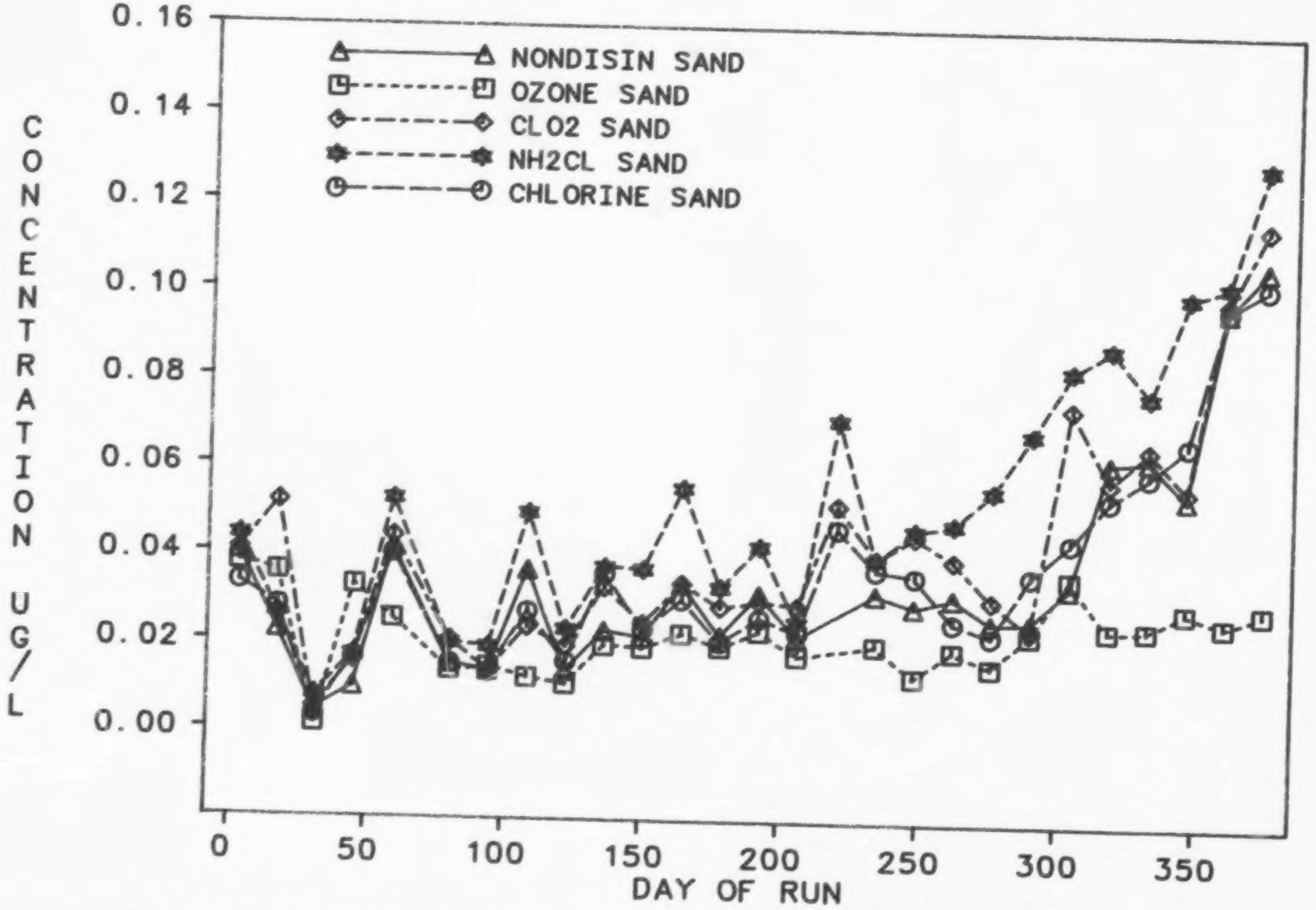


Figure 92. Comparison of the Total Alkane Sand Effluent Levels for each Process Stream.

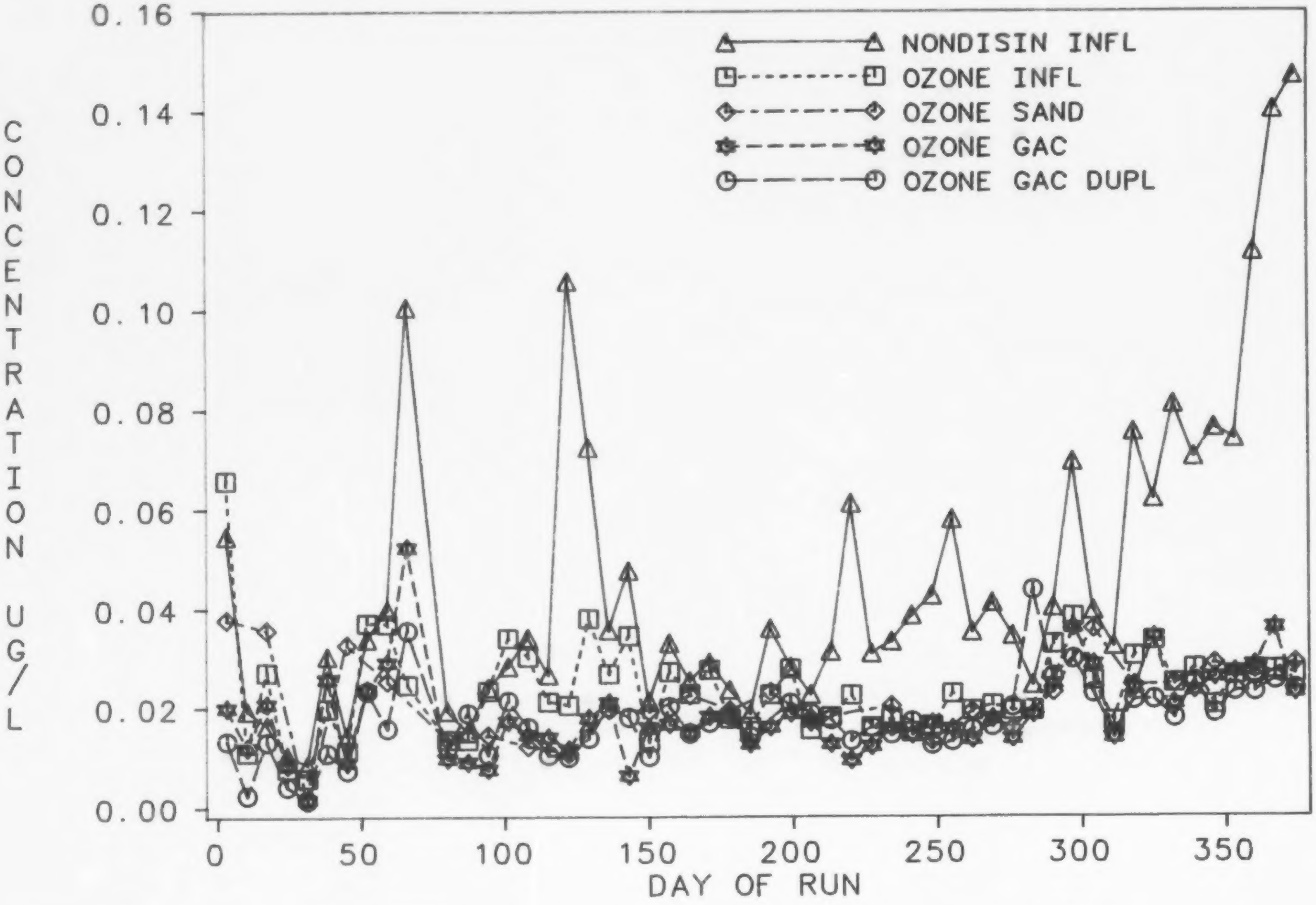


Figure 93. Total Alkane Breakthrough Profiles for the Ozone Process Stream.

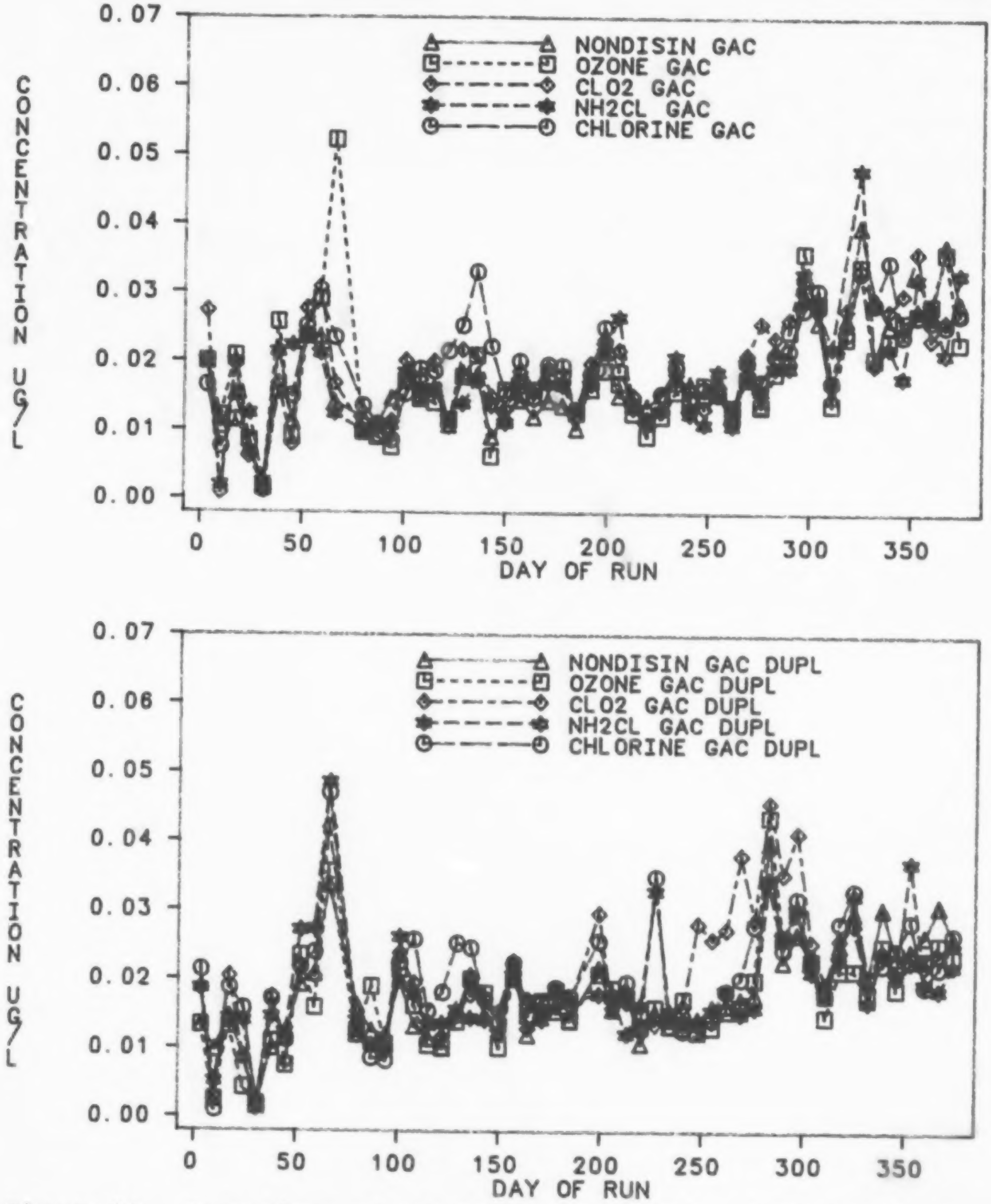


Figure 94. Comparison of the Total Alkane GAC and GAC Duplicate Effluent Levels for each Process Stream.

TABLE 26: FREQUENCY OF OCCURRENCE AND CONCENTRATION RANGES OF NORMAL ALKANES IN THE NONDISINFECTED INFLUENT COMPRISING TOTAL ALKANE

NORMAL ALKANES	FREQUENCY (%)	CONCENTRATION (NG/L)		
		MIN.	AVE.	MAX
decane	87	0.21	2.19	18.0
undecane	89	0.01	1.59	4.93
dodecane	96	0.24	3.23	14.3
pentadecane	94	0.29	5.34	17.5
hexadecane	92	1.29	5.73	15.5
heptadecane	98	5.21	11.1	31.1
nonadecane	96	1.11	3.21	8.03
eicosane	70	1.80	33.6	114

indicating similiar reductions with respect to the nondisinfected influent. Average removals ranging from 44-52% were observed with the nondisinfected and ozone process streams having the higher removals and the chlorinated disinfectant process streams having the lower removals. A typical profile of GAC removal of total alkanes for all process streams, except that of the ozone system, is presented in Figure 95 for the chlorine process stream. As was the case for ozonation, higher GAC removals occurred during the latter part of the operational period when total alkane levels in the nondisinfected influent began to increase. Again, there were no standard breakthrough curves observed for any of the GAC columns.

TOTAL PHTHALATE

Total phthalate is comprised of those phthalates monitored during the operational period which are listed in Table 27 along with their frequency of occurrence and the minimum, maximum, and average concentrations at which they were detected. Although dipropylphthalate was essentially unconfirmed by GC/MS analysis, the substances which eluted at the same GC retention time was quantitated as dipropylphthalate and report as such. The total phthalate levels in the nondisinfected influent ranged from 0.07 - 0.47 ug/l with an average of 0.18 ug/l. These levels are compared with those of the disinfected influents in Figure 96. Although not immediately apparent in the figure, ozonation produced an average removal of 11%. No significant changes in total phthalate levels occurred for the other disinfectants except for a possible slight increase in the chloramine influent toward the latter part of the operational period. A comparison

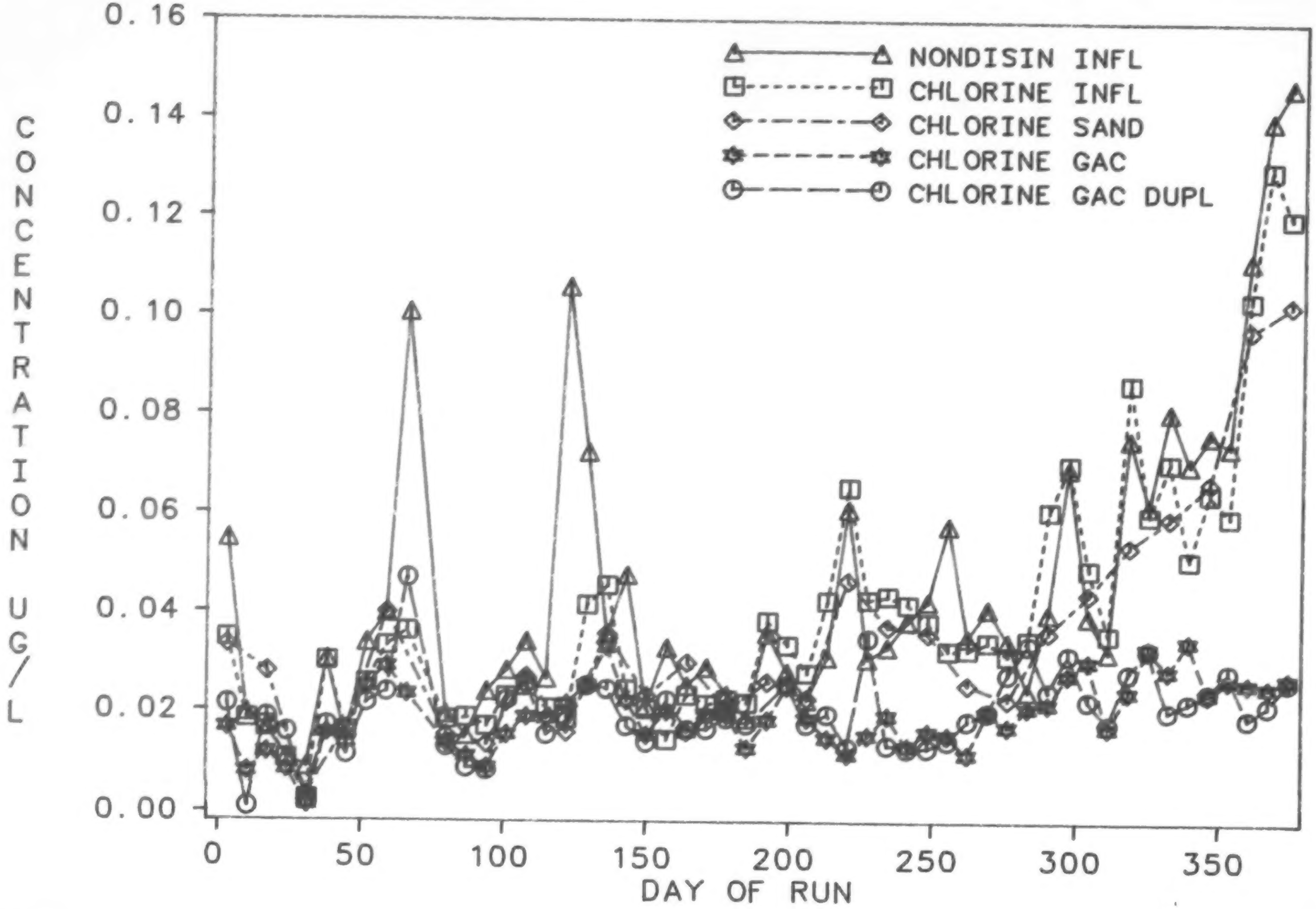


Figure 95. Total Alkane Breakthrough Profiles for the Chlorine Process Stream.

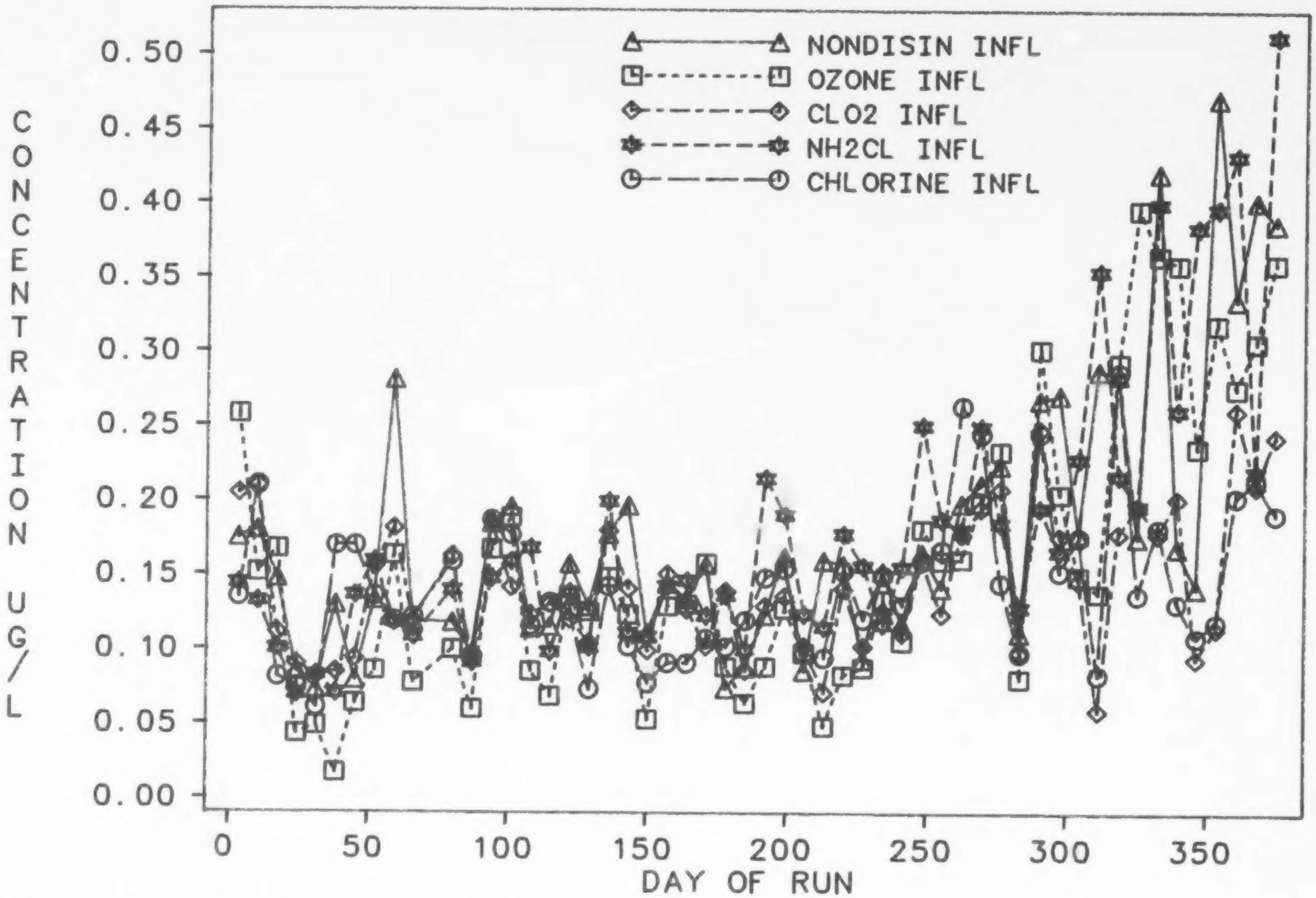


Figure 96. Comparison of the Total Phthalate Influent Levels for each Process Stream.

of the total phthalate levels in the effluents of the sand columns is presented in Figure 97. These levels remained relatively constant and were essentially identical for the nondisinfected, chlorine dioxide, chloramine, and chlorine process streams. Average reductions of 20, 4, 10, 20, & 10% were observed across the sand columns of the nondisinfected, ozone, chlorine dioxide, chloramine and chlorine process streams, respectively. The total phthalate levels in the effluent of the ozone sand column varied from slightly lower than those of the other process streams before day 248 to 0.05 - 0.25 ug/l higher than those of the other process streams after day 248. This increase resulted primarily from increases in dibutylphthalate, diethylphthalate, and bis-2-ethylhexylphthalate. No explanation for this increase was immediately apparent. The effluent levels of total phthalate for the GAC and GAC duplicate columns of each process stream are compared in Figure 98. Similiar effluent concentrations and average removals ranging from 44 - 50% were observed for the GAC columns of each process stream up to day 248. Similiar results were observed for the GAC duplicate columns except that the average removals of the chloramine and chlorine GAC duplicate columns were somewhat lower at 37% and 41%, respectively. After day 248, the data becomes somewhat varied and considerably more erratic. The GAC and sand columns of the nondisinfected process stream showed continued removal as indicated in Figure 99 while the effluent concentrations of the GAC duplicate column were equal to or greater than those of the nondisinfected influent. For the ozone process stream, the effluent concentrations of the GAC, GAC duplicate, and sand columns were equal to or greater than the nondisinfected influent as shown in Figure 100. Except for a few excursions of effluent

TABLE 27 FREQUENCY OF OCCURRENCE AND CONCENTRATION RANGES OF PHTHALATES IN THE NONDISINFECTED INFLUENT COMPRISING TOTAL PHTHALATE.

PHTHALATE	FREQUENCY %	DETECTED CONCENTRATION (NG/L) MIN	AVE	MAX
diethylphthalate	96	28.1	53.7	98.6
dipropylphthalate	49	0.62	3.38	11.4
diisobutylphthalate	98	2.45	6.89	14.5
dibutylphthalate	98	17.5	72.1	362
1,2-butylbenzylphthalate	92	2.38	10.1	32.0
bis-2-ethylhexylphthalate	77	0.59	4.54	29.7
dioctylphthalate	94	4.18	34.0	103

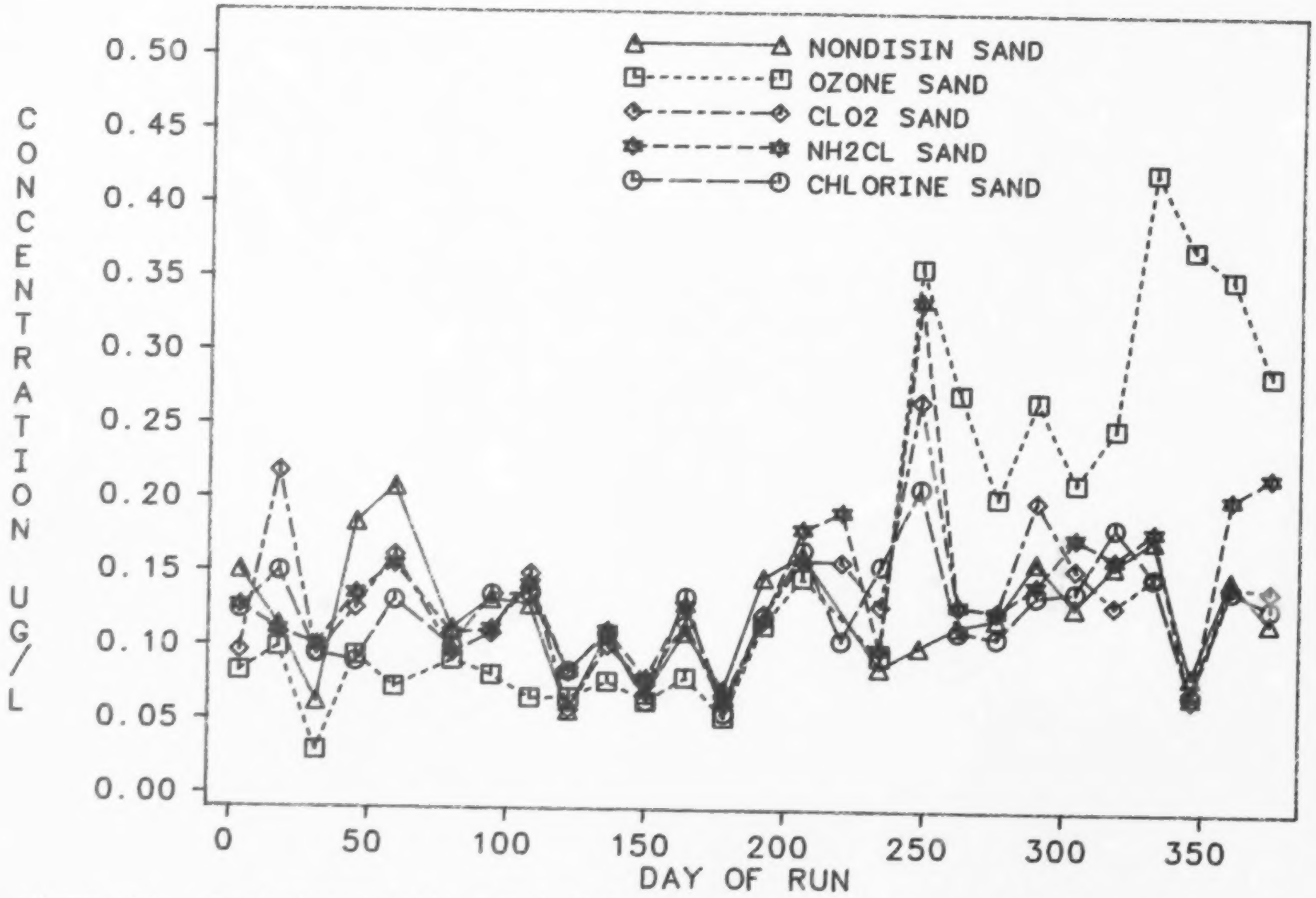


Figure 97. Comparison of the Total Phthalate Sand Effluent Levels for each Process Stream.

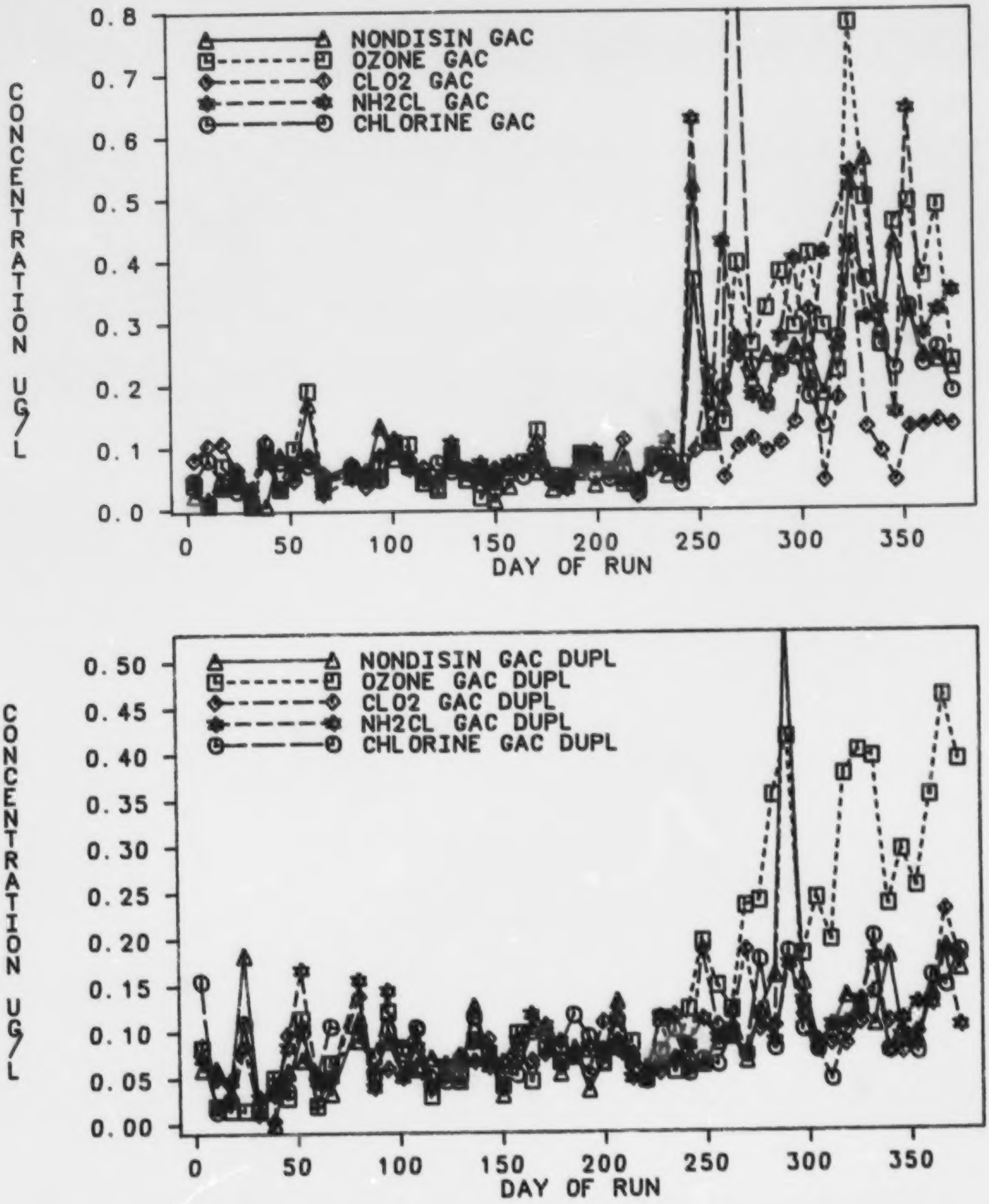


Figure 98. Comparison of the Total Phthalate GAC and GAC Duplicate Effluent Levels for each Process Stream.

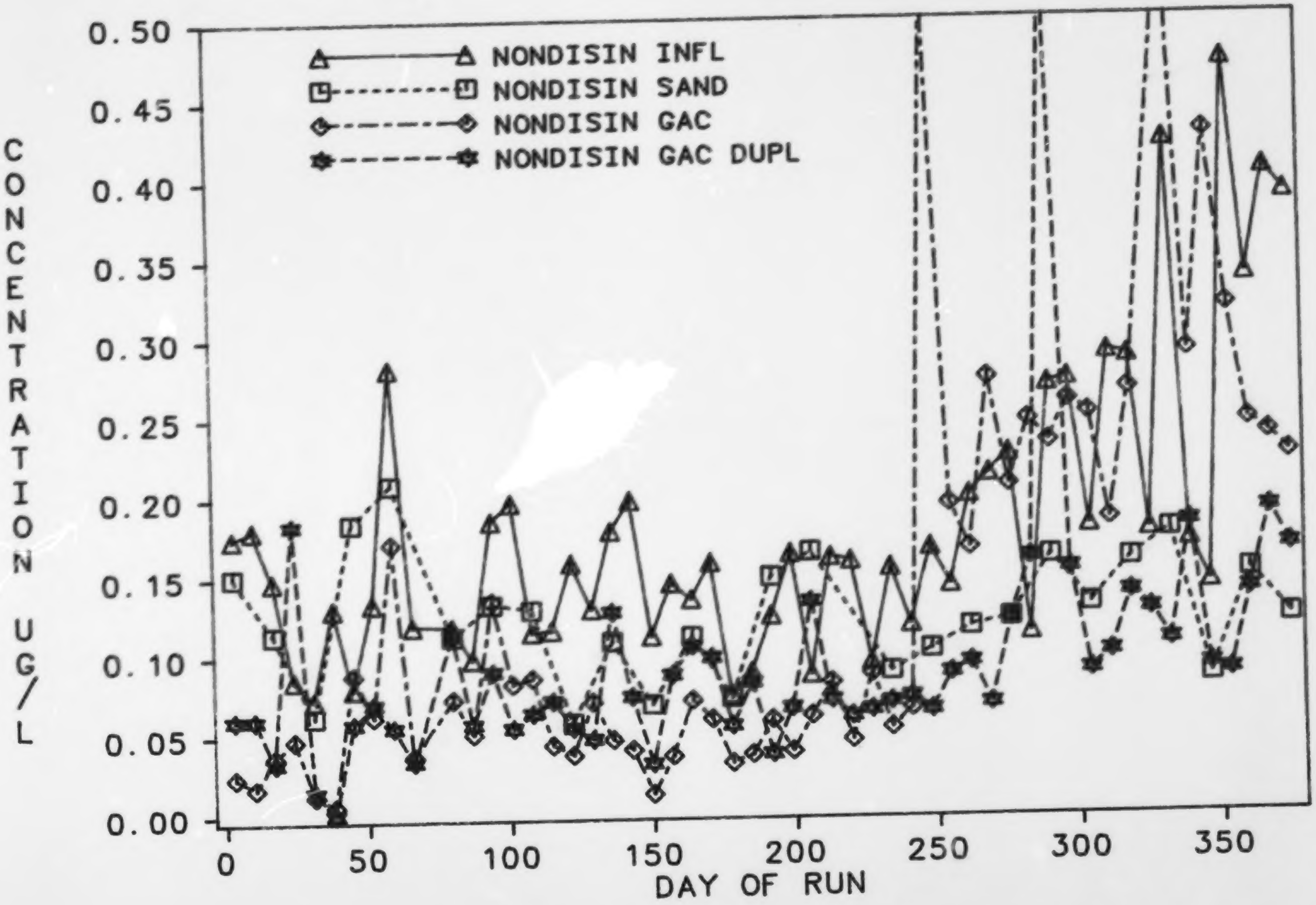


Figure 99. Total Phthalate Breakthrough Profiles for the Nondisinfected Process Stream.

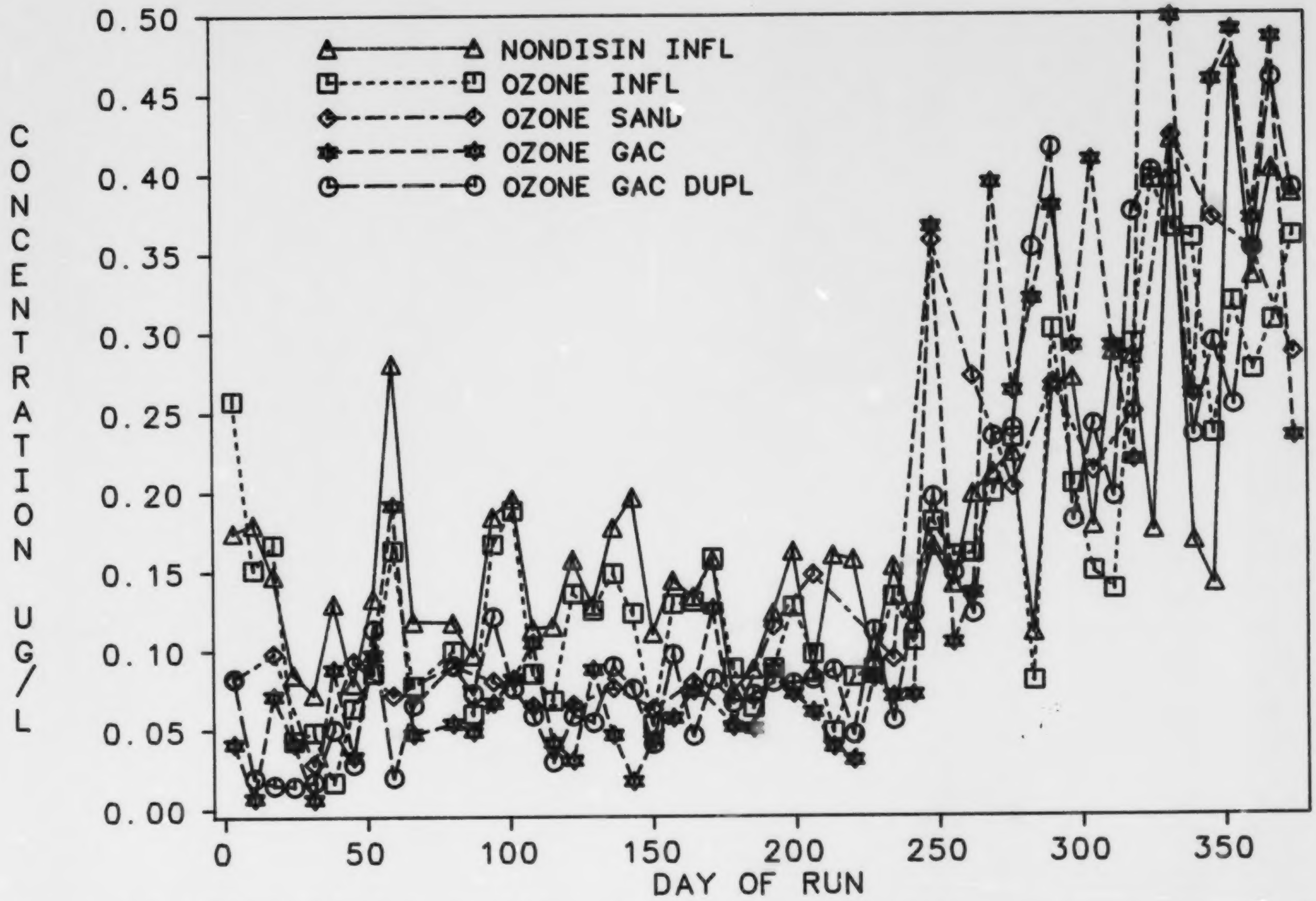


Figure 100. Total Phthalate Breakthrough Profiles for the Ozone Process Stream.

concentration above that of the nondisinfected influent, continued removal was evident for the GAC, GAC duplicate, and sand columns of the chlorine dioxide process stream as indicated in Figure 101. Both the chloramine and chlorine process streams exhibited similiar variations in Figure 102 with the sand and GAC duplicate columns showing continued removal while the effluent concentrations of the GAC columns were equivalent to or greater than the nondisinfected influent. These variations were produced primarily by the same phthalates which were responsible for the variations observed in the ozone sand column as previously indicated. As with the ozone sand column, no immediate explanation for these variations were evident.

TOTAL POLYNUCLEAR AROMATIC HYDROCARBON (PNAH)

Total PNAH is the summation of all of the polynuclear aromatic hydrocarbons listed in Table 28 which includes their minimum, maximum, and average concentrations at which they were detected and their frequency of occurrance at which they were detected in the nondisinfected influent. The total PNAH concentrations in the nondisinfected influent which averaged 144ng/l with a range of 38-550ng/l, are compared to those of the disinfected influents in Figure 103. An average removal of 74% was observed for ozonation with the other disinfectants producing no significant reduction. A comparison of the total PNAH levels in the effluents of the sand columns of each process stream in Figure 104 indicated that a reduction averaging 49% was observed across the nondisinfected sand column. This reduction of total PNAH was attributable to biodegradation as evidenced by the considerably greater heterotrophic plate count in the effluent of the nondisinfected sand column. Significant levels of biodegradation of PNAHs as well as other organic substances have also been reported by Fochtman.[8] There were no significant reductions observed across the sand columns of the disinfected process streams. The lower concentrations in the ozone sand column effluent were attributable to ozonation as indicated in Figure 105. This figure shows that the influent and effluent levels of the ozone sand column were essentially identical as were those of the GAC and GAC duplicate columns indicating that no further reduction of total PNAH occurred across either GAC column. The total PNAH levels in the effluent of the GAC and GAC duplicate columns are compared in Figure 106 which indicates that essentially, identical reductions, which averaged 72-77%, were observed for all process streams relative to the nondisinfectant influent. Thus, it is evident that ozonation produced the same level of total PNAH removal as did GAC filtration. The breakthrough profiles of the nondisinfected GAC and GAC duplicate columns are presented in Figure 107 while those typical of the chlorinated process streams are presented in Figure 108 for the chlorine dioxide process stream. The breakthrough profiles of

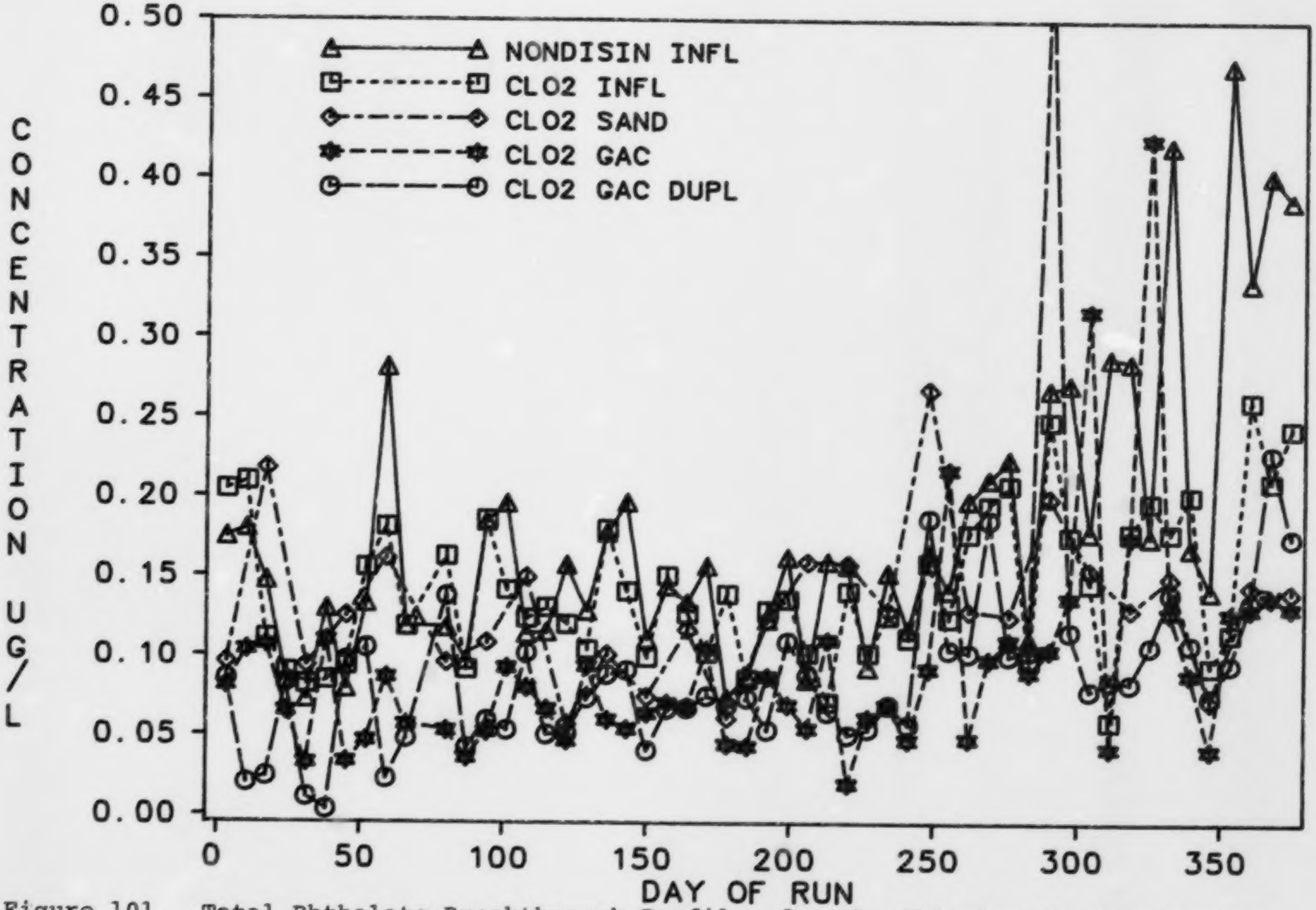
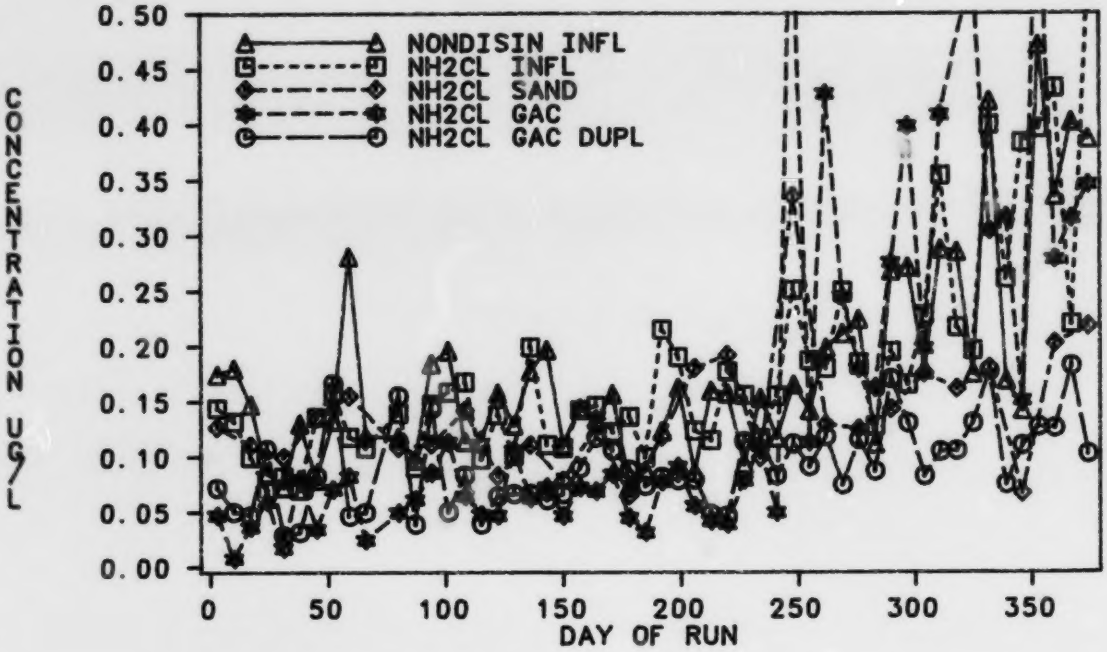


Figure 101. Total Phthalate Breakthrough Profiles for the Chlorine Dioxide Process Stream.



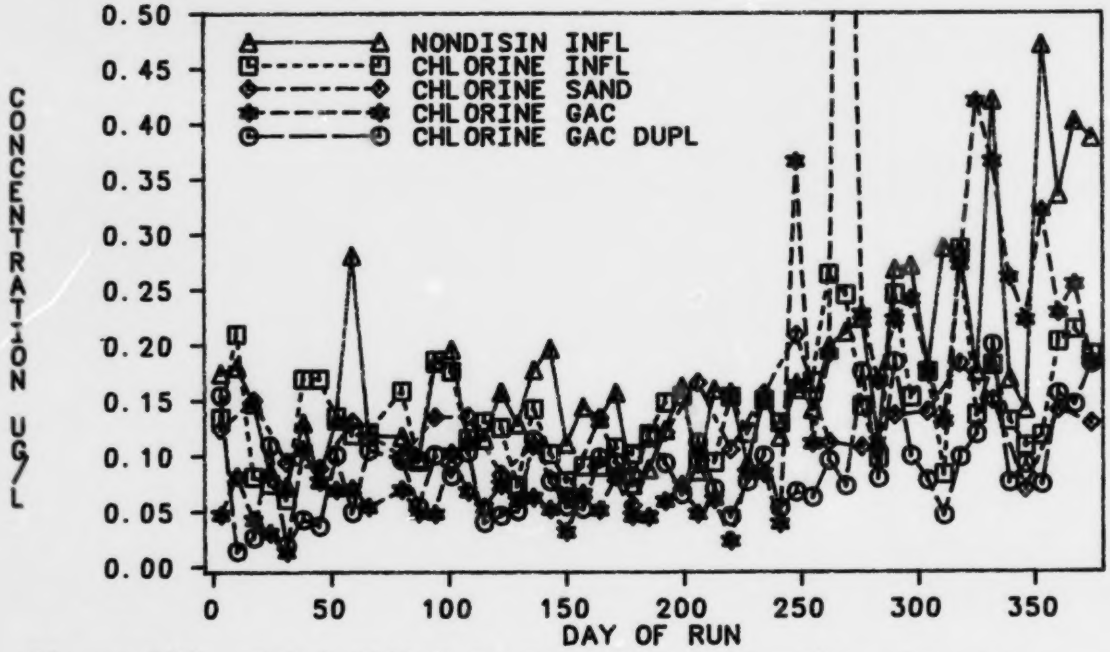


Figure 102. Total Phthalate Breakthrough Profiles for the Chloramine and Chlorine Process Streams.

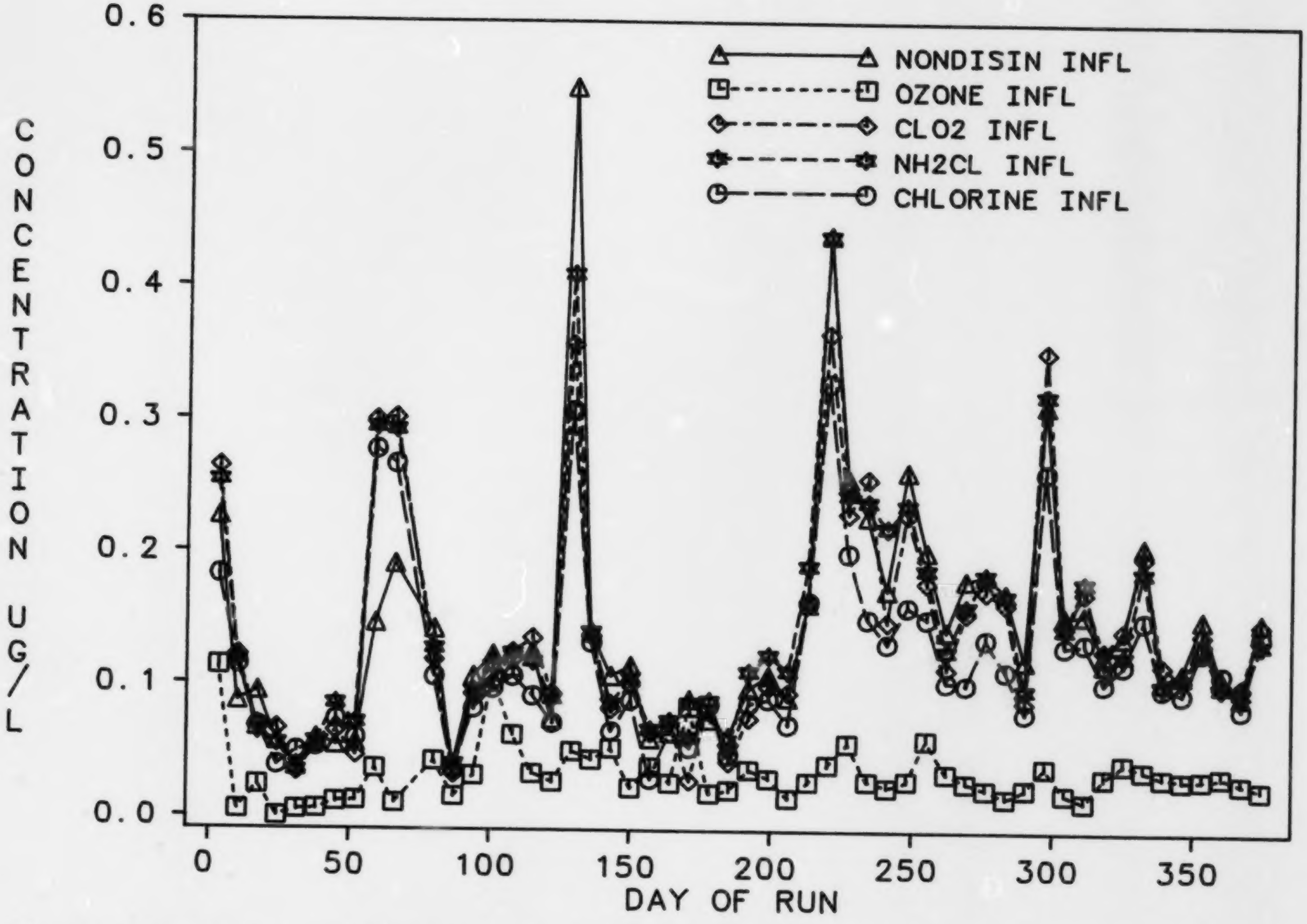


Figure 103. Comparison of the Total PNAH Influent Levels for each Process Stream.

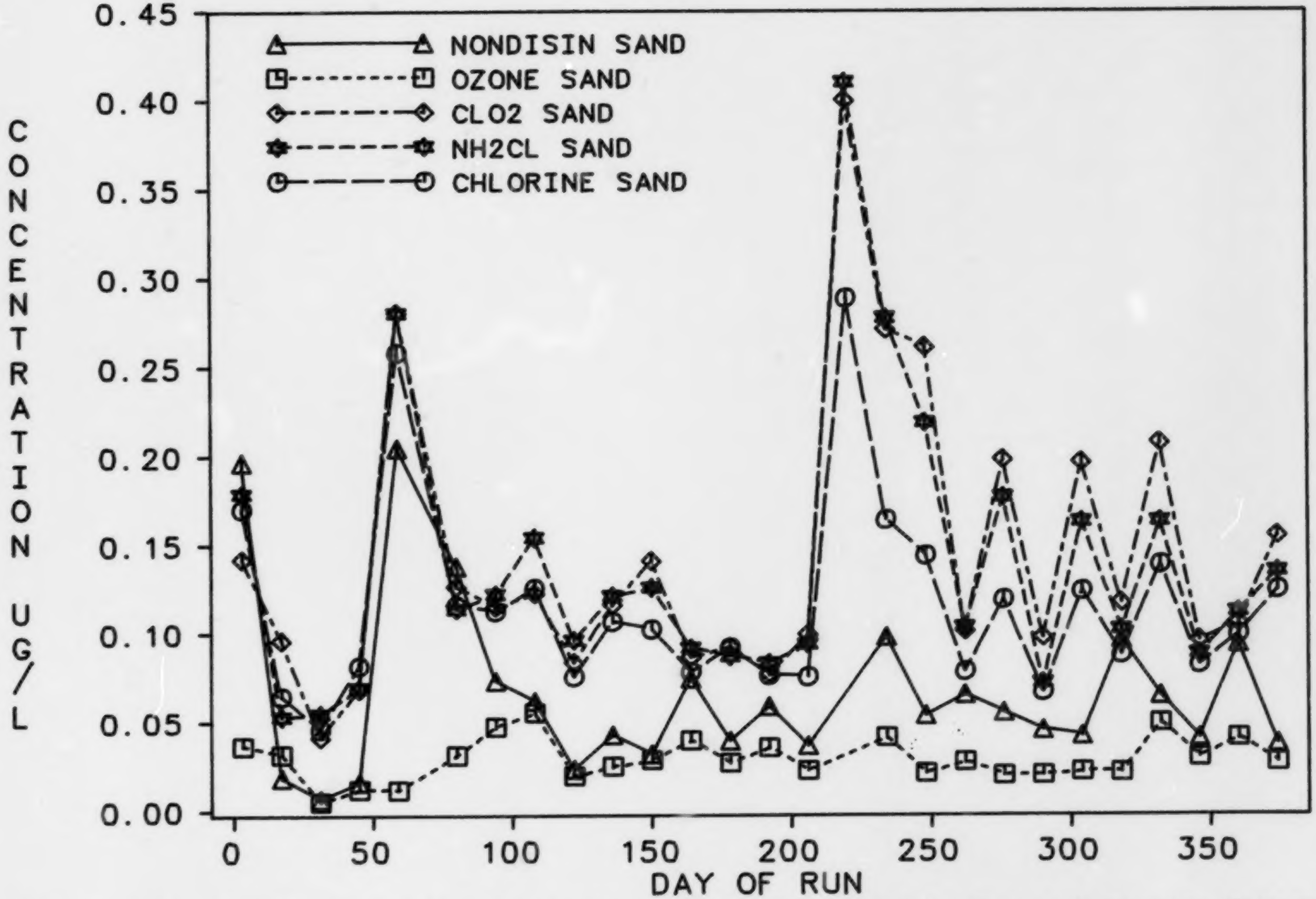


Figure 104. Comparison of the Total PNAH Sand Effluent Levels for each Process Stream.

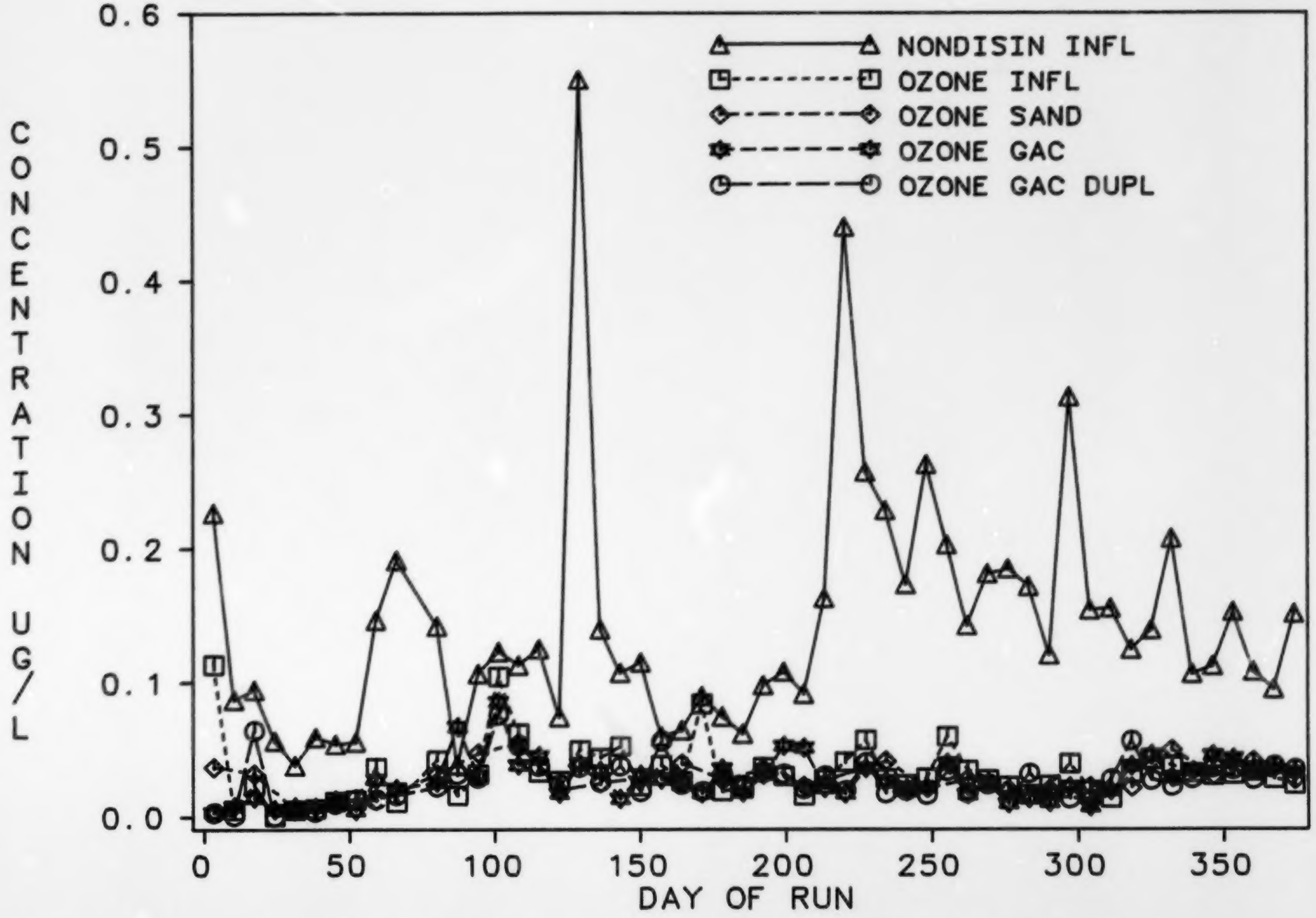


Figure 105. Total PNAH Breakthrough Profiles for the Ozone Process Stream.

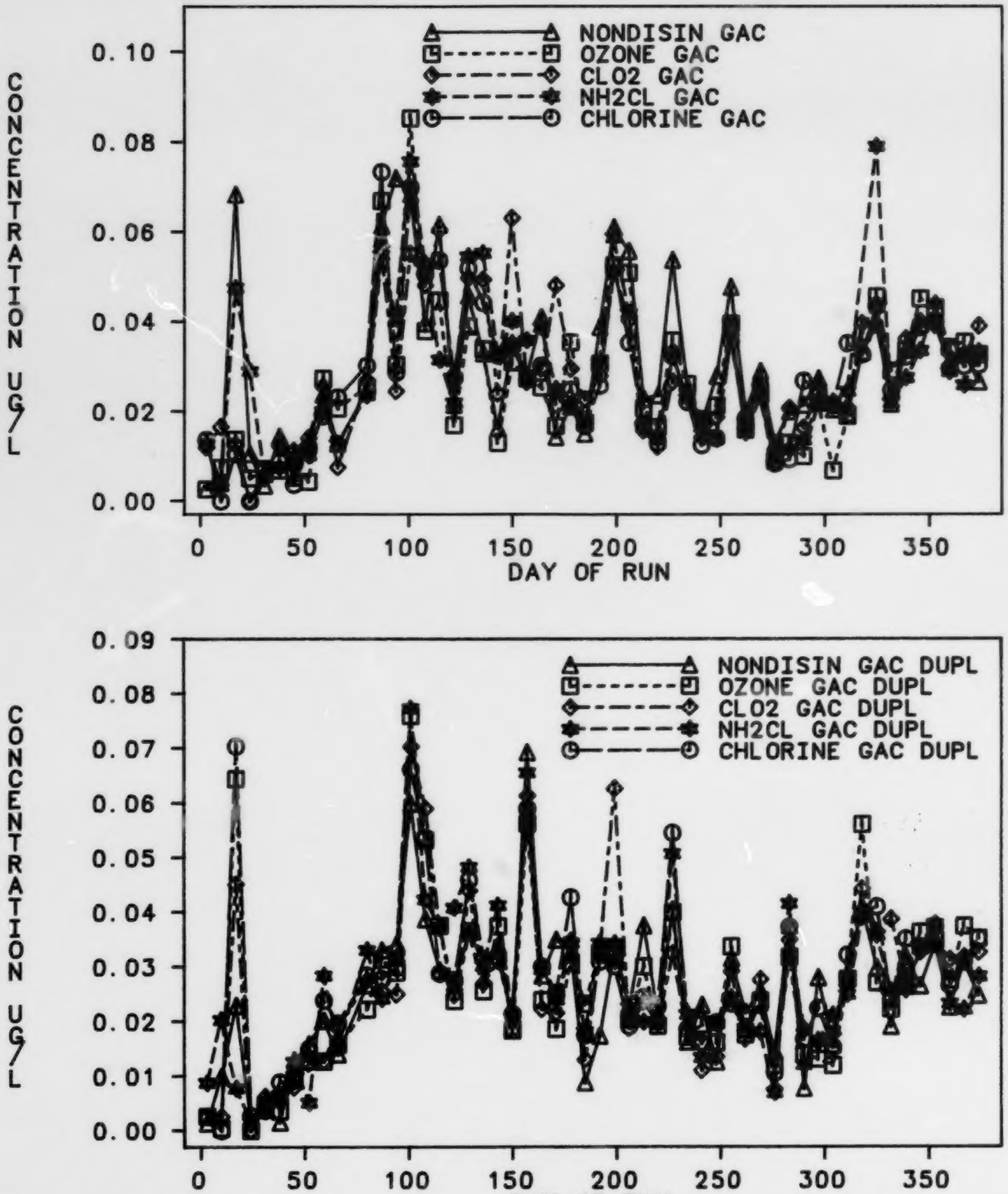


Figure 106. Comparison of the Total PNAH GAC and GAC Duplicate Effluent Levels for each Process Stream.

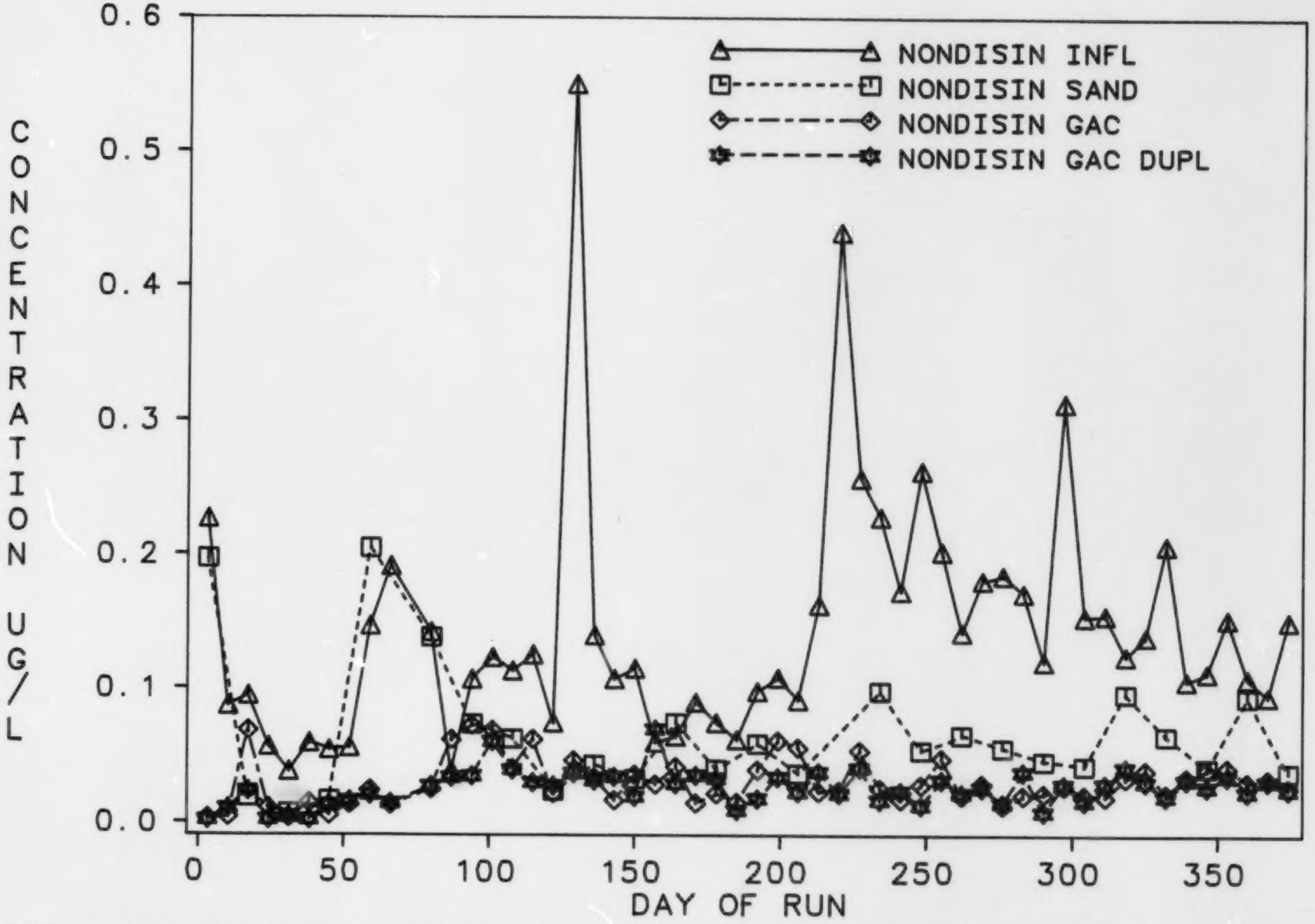


Figure 107. Total PNAH Breakthrough Profiles for the Nondisinfected Process Stream.

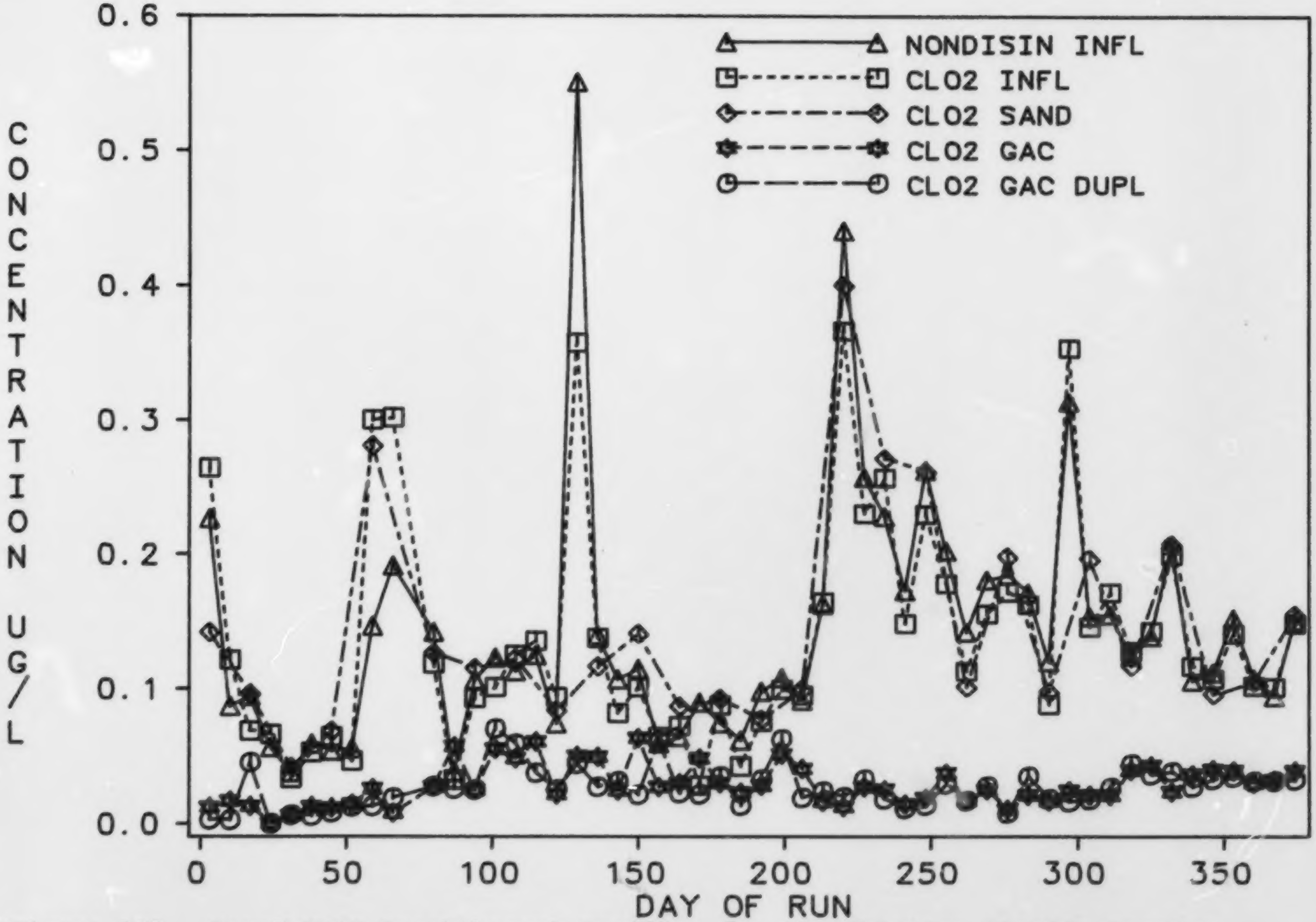


Figure 108. Total PNAH Breakthrough Profiles for the Chlorine Dioxide Process Stream.

TABLE 28. FREQUENCY OF OCCURRANCE AND CONCENTRATION RANGES OF PNAHS IN THE NONDISINFECTED INFLUENT COMPRISING TOTAL PNAH.

PNAHs	FREQUENCY (%)	CONCENTRATION (NG/L)		
		MIN.	AVE.	MAX.
indene	83	0.12	4.0	16.9
tetralin	98	0.45	8.3	29.9
naphthalene	98	4.6	16.3	67.8
2-methylnaphthalene	100	5.8	24.7	93.5
1-methylnaphthalene	100	3.0	13.3	51.3
cyclohexylbenzene	91	0.1	5.3	21.3
biphenyl	85	0.6	4.2	17.8
2-ethylnaphthalene	91	1.0	10.7	49.2
2,6-dimethylnaphthalene	89	1.8	14.4	59.1
2,3-dimethylnaphthalene	92	1.3	8.1	29.4
1,2-dimethylnaphthalene	87	2.9	19.3	67.1
acenaphthene	100	2.0	7.9	30.3
fluorene	87	1.0	5.3	30.7
phenanthrene	92	1.3	10.7	36.2
anthracene	81	0.1	2.9	38.3
fluoranthene	74	0.6	4.4	9.7
pyrene	81	0.5	6.1	22.4

each process stream indicate that there was no specific breakthrough of total PNAH throughout the operational period. These profiles also suggest that a significant portion of the total PNAH removal observed across the GAC columns appeared to be attributable to biological degredation as indicated by the reductions observed across the control sand column.

TOTAL CHLOROBENZENE

Total chlorobenzene is comprised of those chlorobenzenes listed in Table 29 which were monitored during the operational period. The total chlorobenzene levels in the nondisinfected influent ranged from 0.004-0.304 ug/l with an average of 0.10 ug/l. The influent levels of total chlorobenzene of each process stream are compared in Figure 109. A 68% average reduction was observed for ozonation with respect to the nondisinfected influent while disinfection with free chlorine resulted in an average increase of 75%. The total chlorobenzene levels in the nondisinfected influent were essentially unaffected by chlorine dioxide and chloramination. The formation of chlorobenzenes following chlorination will be discussed in greater detail in a later section covering disinfection byproducts. Comparison of

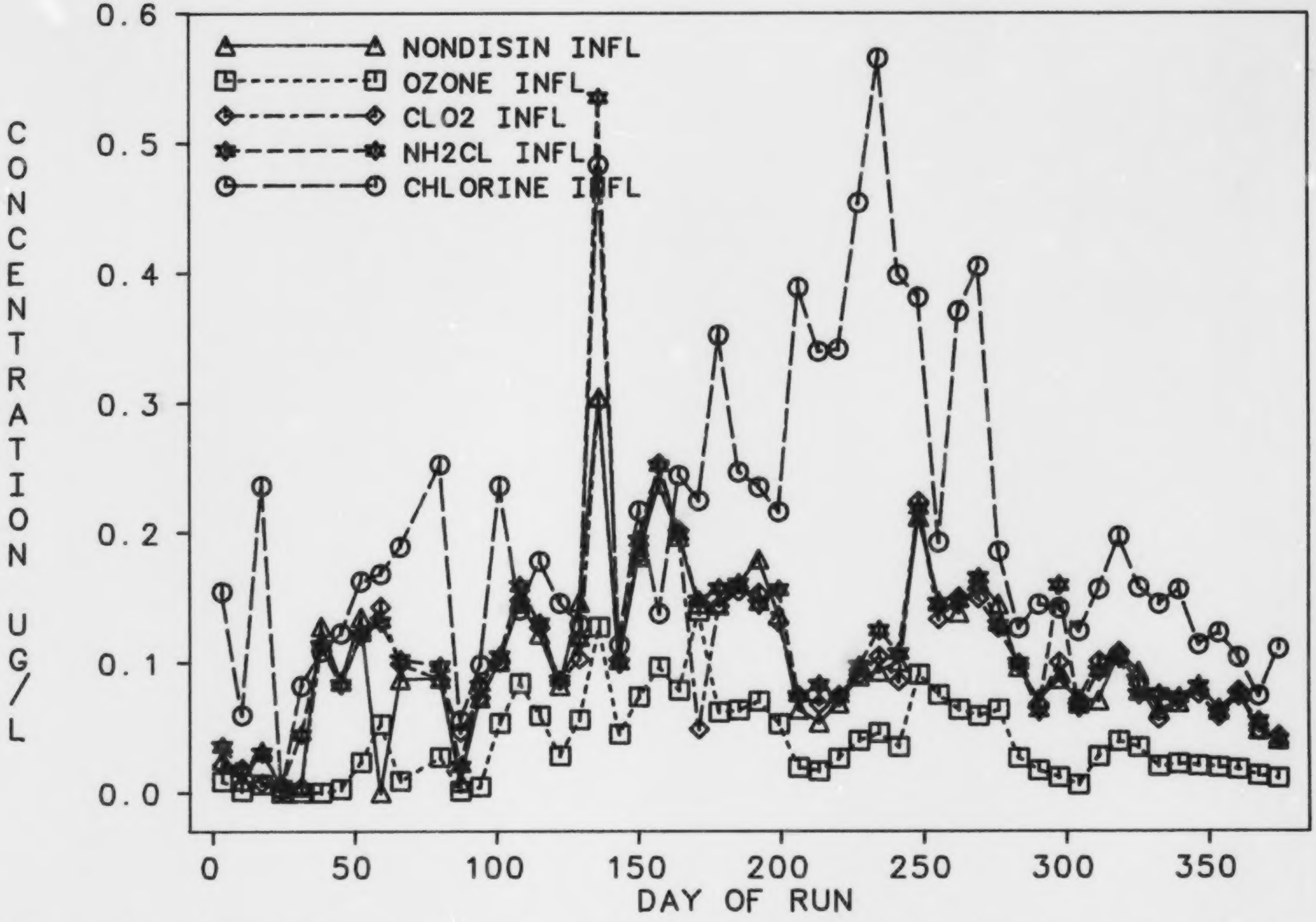


Figure 109. Comparison of the Total Chlorobenzene Influent Levels for each Process Stream.

TABLE 29 FREQUENCY OF OCCURRENCE AND CONCENTRATION RANGES OF CHLOROBENZENES IN THE NONDISINFECTED INFLUENT COMPRISING TOTAL CHLOROBENZENE.

		DETECTED CONCENTRATION (NG/L)		
CHLOROBENZENE	FREQUENCY %	MIN	AVE	MAX
1,2-dichlorobenzene	89	0.73	7.54	24.0
1,3-dichlorobenzene	54	0.05	1.89	8.00
1,4-dichlorobenzene	94	1.41	9.85	62.1
1,2,4-trichlorobenzene	72	0.61	6.20	20.2
1-chloro-2-nitrobenzene	91	5.91	26.2	80.5
1-chloro-4-nitrobenzene	91	0.48	61.2	214

the total chlorobenzene levels in the effluents of the sand columns in Figure 110 shows that an average reduction of 26% was observed across the chlorine sand column. However, these levels remained an average of 43% greater than that of the nondisinfected influent as can be seen in Figure 111. As with previous parameters, the lower total chlorobenzene concentrations observed for the ozone sand column were attributable to ozonation as indicated in Figure 112. Comparisons of the total chlorobenzene levels in the effluents of the GAC and GAC duplicate column are presented in Figure 113. As indicated by the similiar effluent concentrations, similiar removals of total chlorobenzene were observed for all GAC columns ranging from93-95%. Thus, despite a 75% increase of total chlorobenzenes in the chlorine influent, GAC filtration with a 20 minute EBCT was capable of producing equivalent reductions in total chlorobenzenes as those observed for the other process streams relative to the nondisinfected influent. A profile of GAC removals of total chlorobenzene for the chlorine dioxide process stream is presented in Figure 114. This profile is also typical of the nondisinfected and chloramine GAC columns relative to the removal of total chlorobenzene. As with the other semivolatile parameters previously examined, no standard breakthrough curves were observed for any of the GAC columns.

TOTAL NITROBENZENE

Total nitrobenzene is derived from the summation of nitrobenzene, 2-nitrotoluene, and 2,4-dinitrotoluene. The frequencies of occurrance of these substances in the nondisinfected influent were 54, 94, and 89%, respectively. The minimum, average, and maximum detected concentrations of nitrobenzene in the nondisinfected influent were 1.1, 9.5, and 53

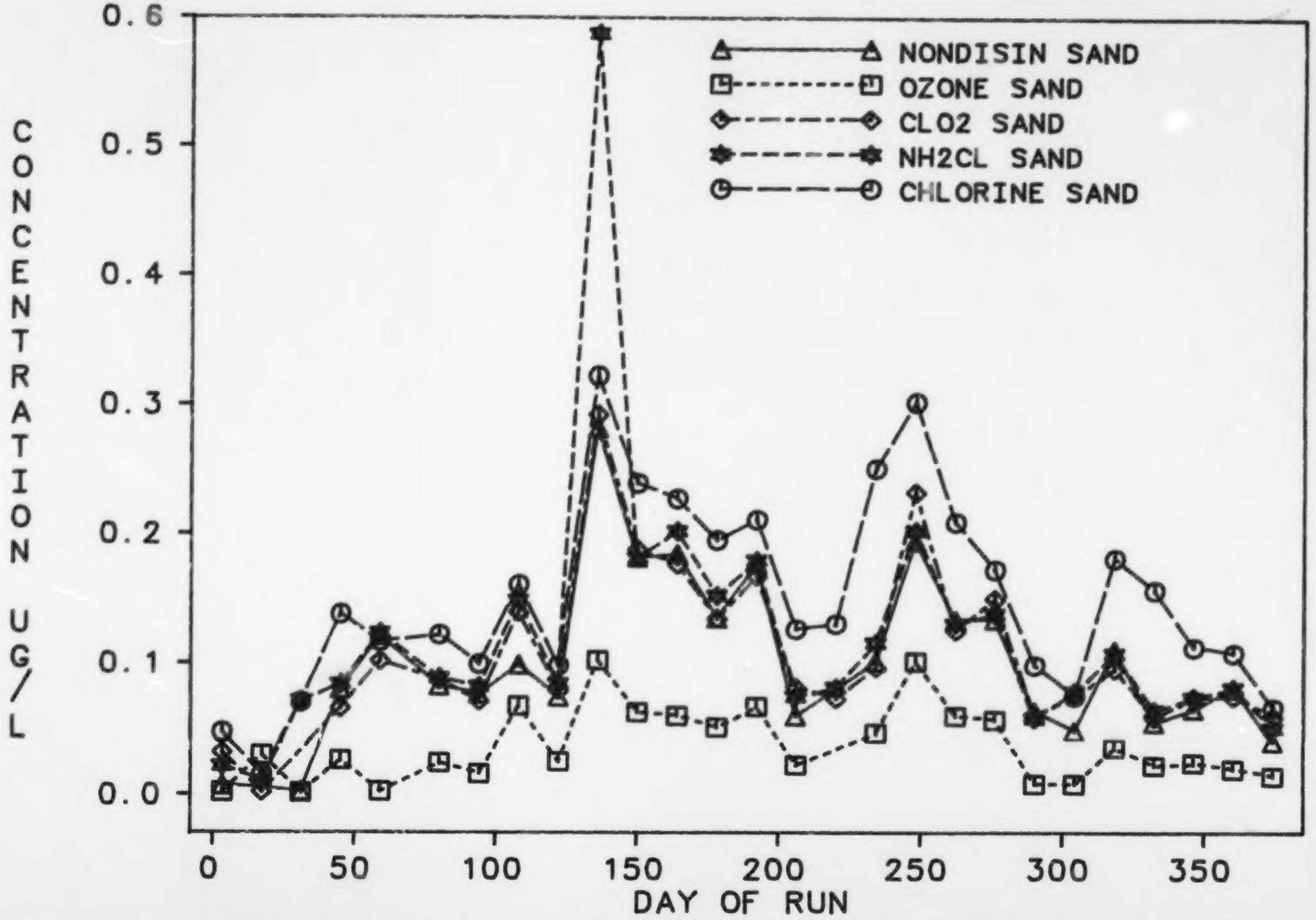


Figure 110. Comparison of the Total Chlorobenzene Sand Effluent Levels for each Process Stream.

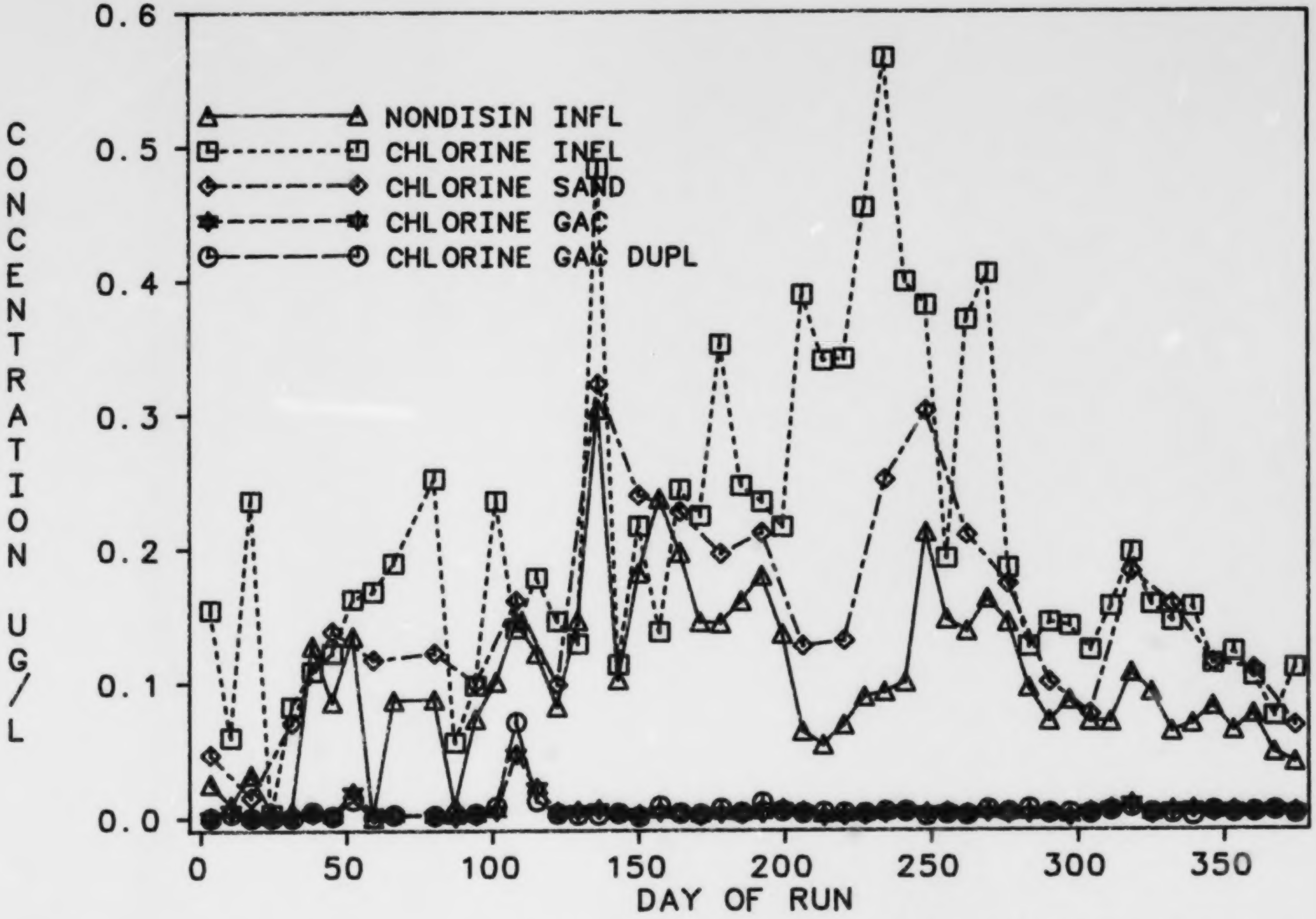


Figure 111. Total Chlorobenzene Breakthrough Profiles for the Chlorine Process Stream.

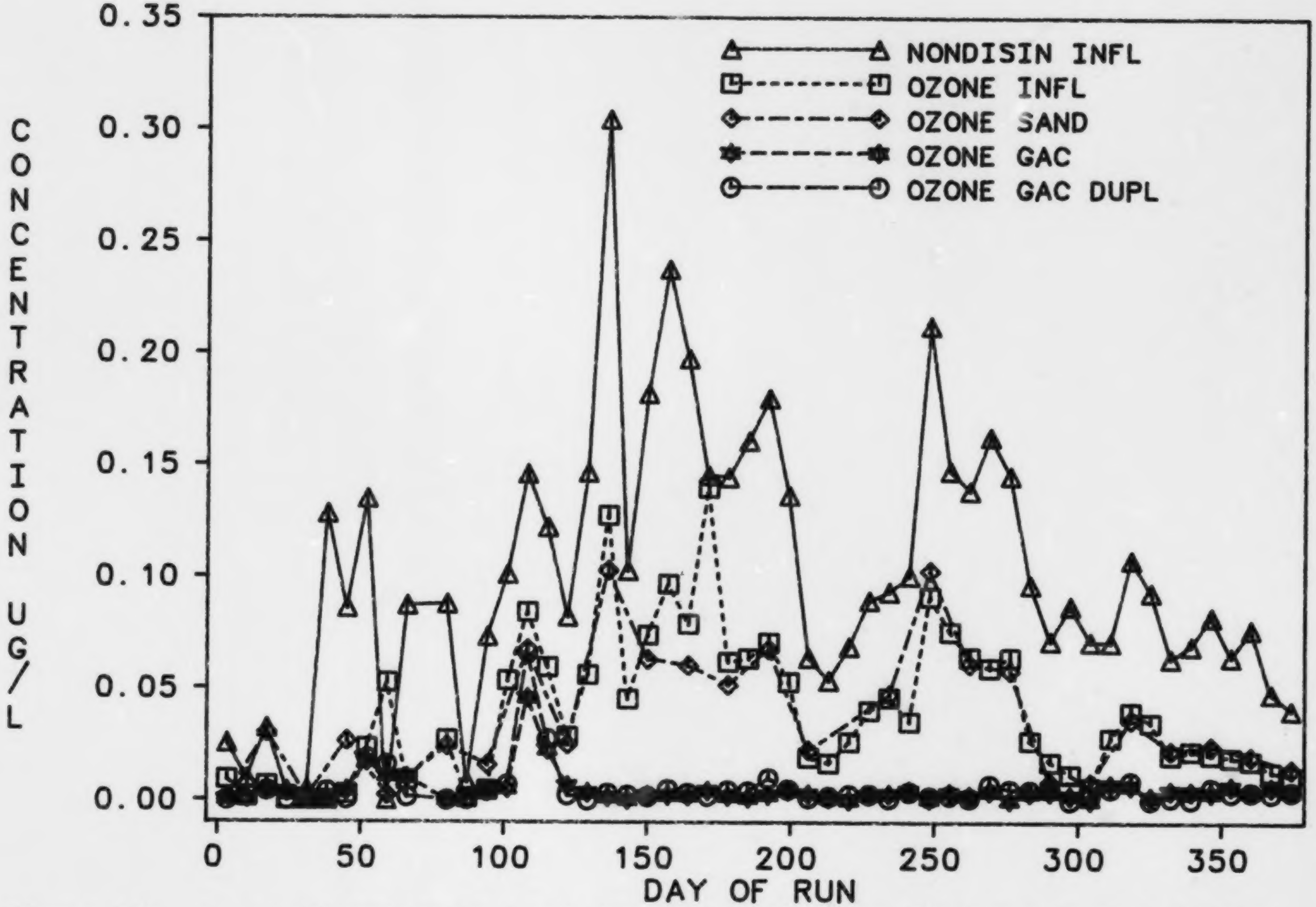


Figure 112. Total Chlorobenzene Breakthrough Profiles for the Ozone Process Stream.

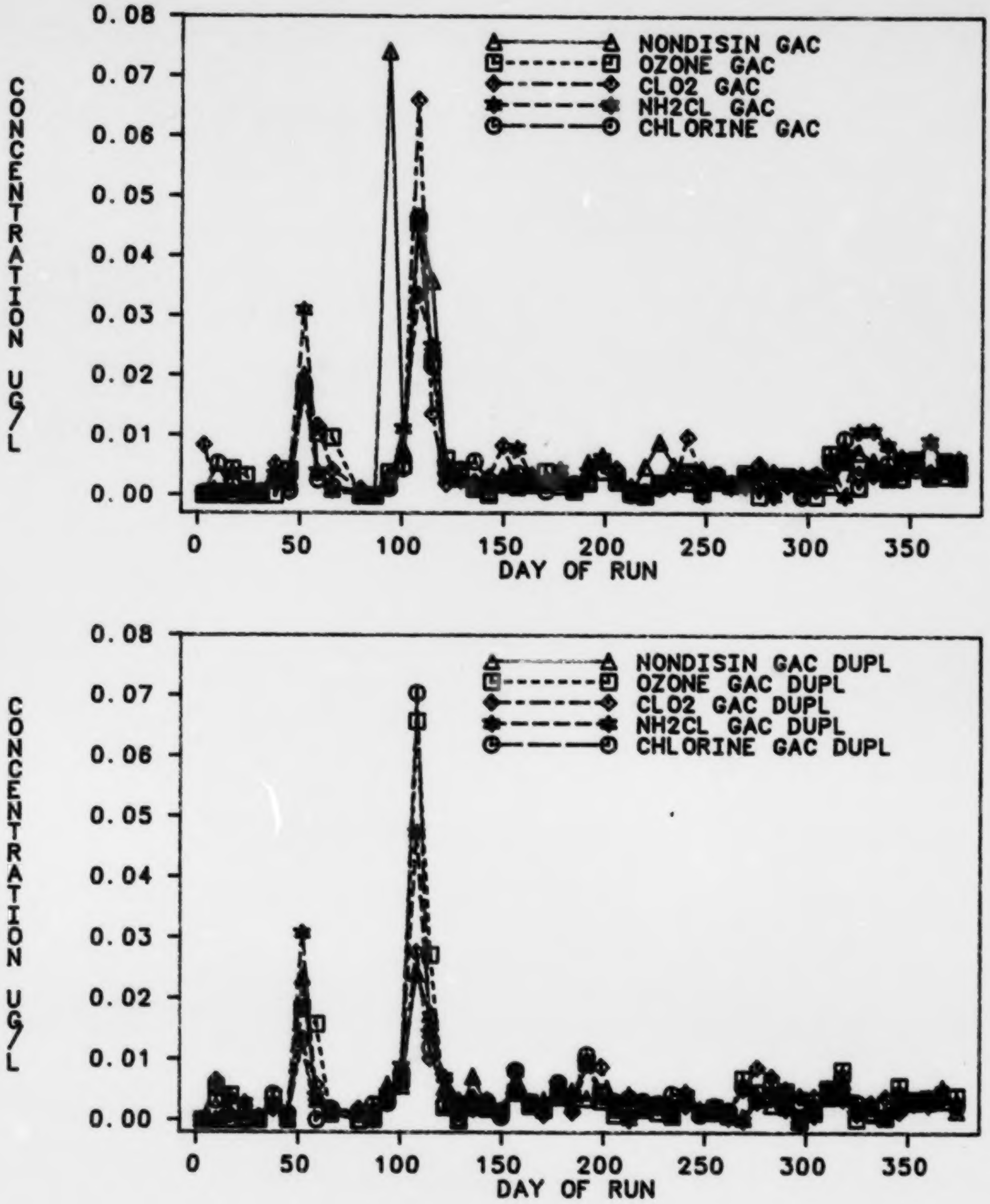


Figure 113. Comparison of the Total Chlorobenzene GAC and GAC Duplicate Effluent Levels for each Process Stream.

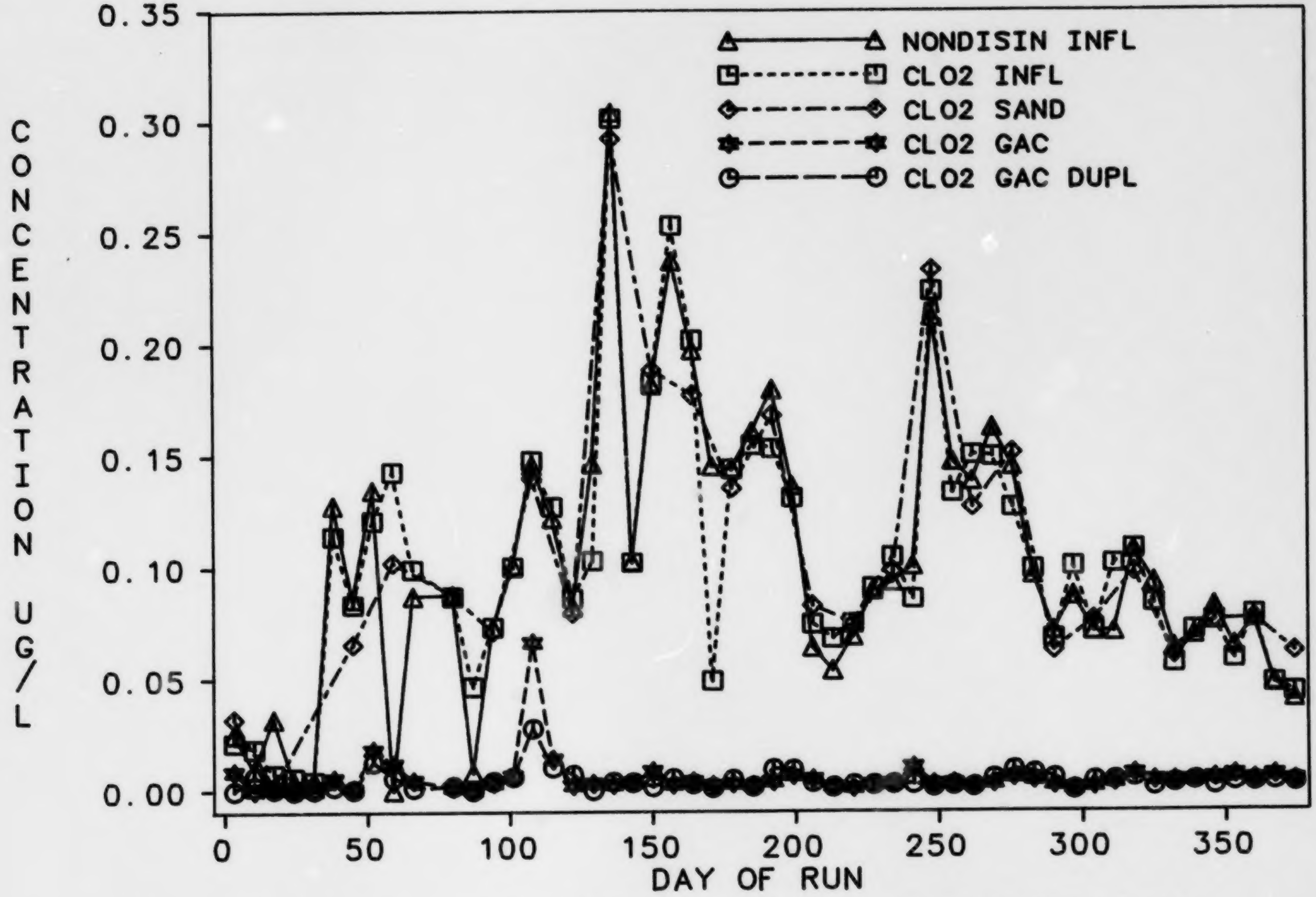


Figure 114. Total Chlorobenzene Breakthrough Profiles for the Chlorine Dioxide Process Stream.

ng/l; those of 2-nitrotoluene were 0.1, 2.6, and 5.6 ng/l; and those of 2,4-dinitrotoluene were 0.9, 18, and 260 ng/l. The levels of total nitrobenzene in the nondisinfected influent are compared to those of the disinfected process streams in Figure 115. An average reduction of 61% was observed across the operational period for ozonation while chlorination resulted in an average increase of 43% after day 100. Prior to day 100, little to no increase was observed. The total nitrobenzene levels in the effluent of the sand column of each process stream are compared in Figure 116. These levels are essentially identical to their respective influent concentrations thus indicating that there was no removal of total nitrobenzene across any of the sand columns. The effluent concentrations of total nitrobenzene for the GAC and GAC duplicate columns of each process stream are compared in Figure 117. Although the data are somewhat erratic, essentially the same effluent concentrations were observed for each GAC and GAC duplicate column with average removals ranging from 81 - 92%. Thus, although the influent levels of total nitrobenzene varied somewhat with the chlorine influent having been higher than normal and the ozone influent having been lower, equivalent reductions of total nitrobenzene with respect to the nondisinfected influent occurred across the GAC and GAC duplicate columns of each process stream. There were no breakthrough curves observed for any of the GAC or GAC duplicate columns as indicated for the chloramine process stream in Figure 118 which depicts the typical removal of total nitrobenzene observed for each process stream.

TOTAL ALKYLALDEHYDE

Only two alkylaldahydes, octanal and nonanal, were quantified using the pentane extraction process previously described. Octanal was observed only 66% of the time in the nondisinfected influent with minimum, average, and maximum detected concentrations of 0.01, 4.7 and 12.0 ng/l, respectively, while that for nonanal, which occurred at a frequency of 89%, was 1.7, 12.7 and 26.8 ng/l. Total alkylaldehyde is the sum of these two constituents which in the nondisinfected influent ranged from below the detection limit to 37.0 ng/l with an average of 14.4 ng/l. The influent levels of total alkylaldehyde for each process stream are compared in Figure 119. An average uniform increase in total alkylaldehyde of 144% was observed for ozonation while a relatively nonuniform increase of 56% occurred for the chlorine system, primarily between day 150 and day 300. Average reductions of 62% and 26% were observed, respectively, across the sand columns of the ozone and chlorine process streams, thus making their effluent concentrations essentially the same as that of the nondisinfected influent as indicated in the upper portion of Figure 120. Essentially no reductions were observed for GAC filtration as typified by the effluents of the

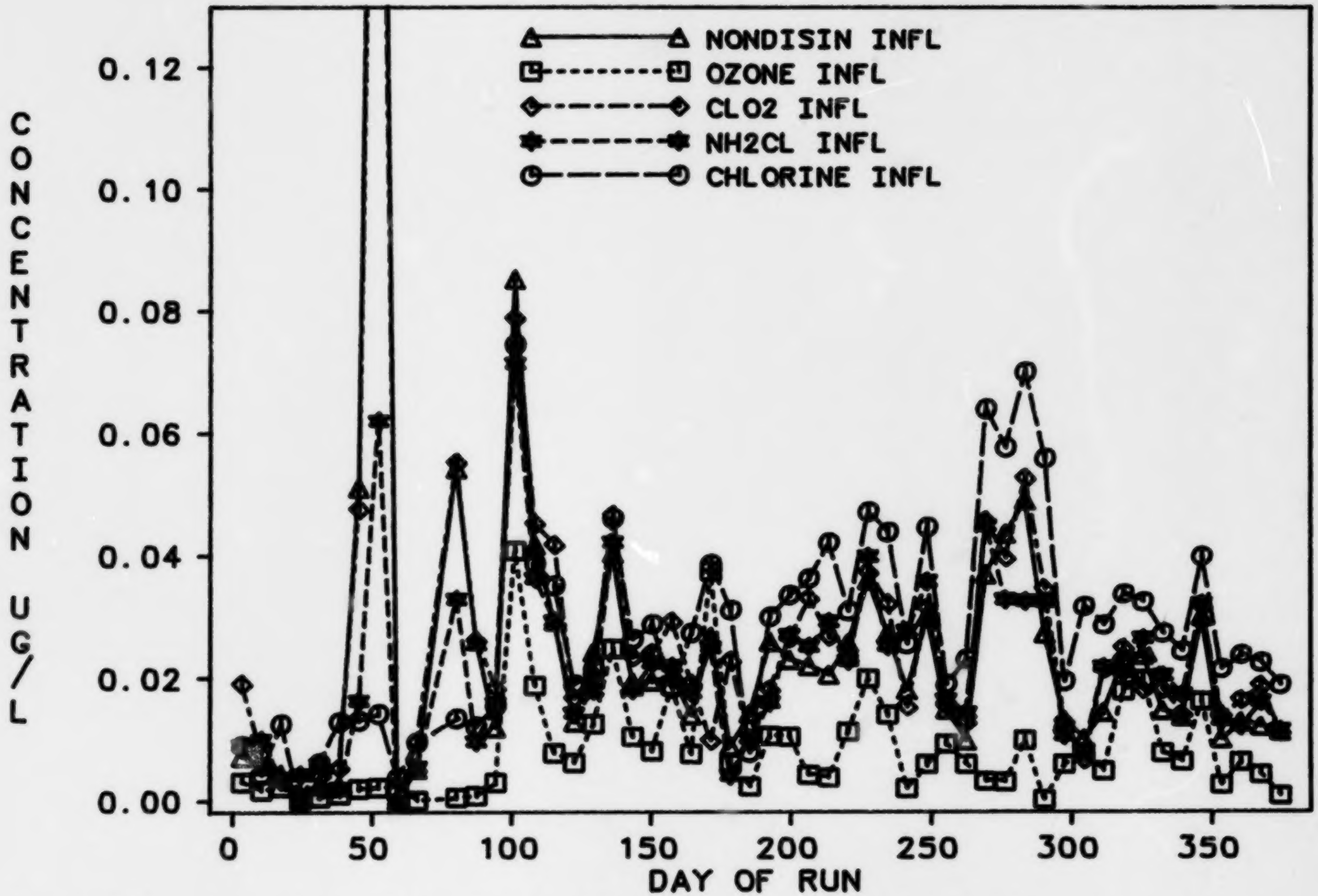


Figure 115. Comparison of the Total Nitrobenzene Influent Levels for each Process Stream.

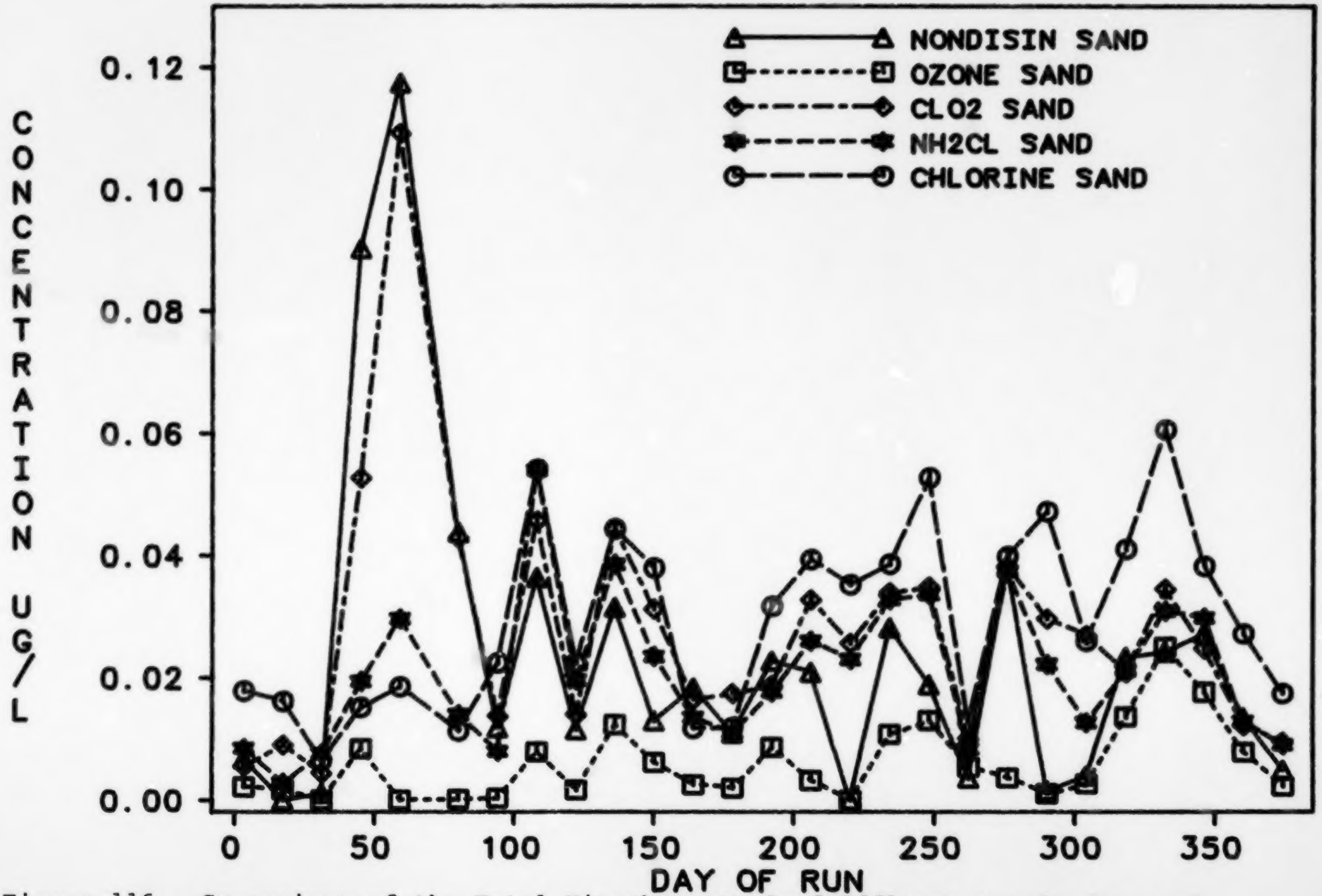


Figure 116. Comparison of the Total Nitrobenzene Sand Effluent Levels for each Process Stream.

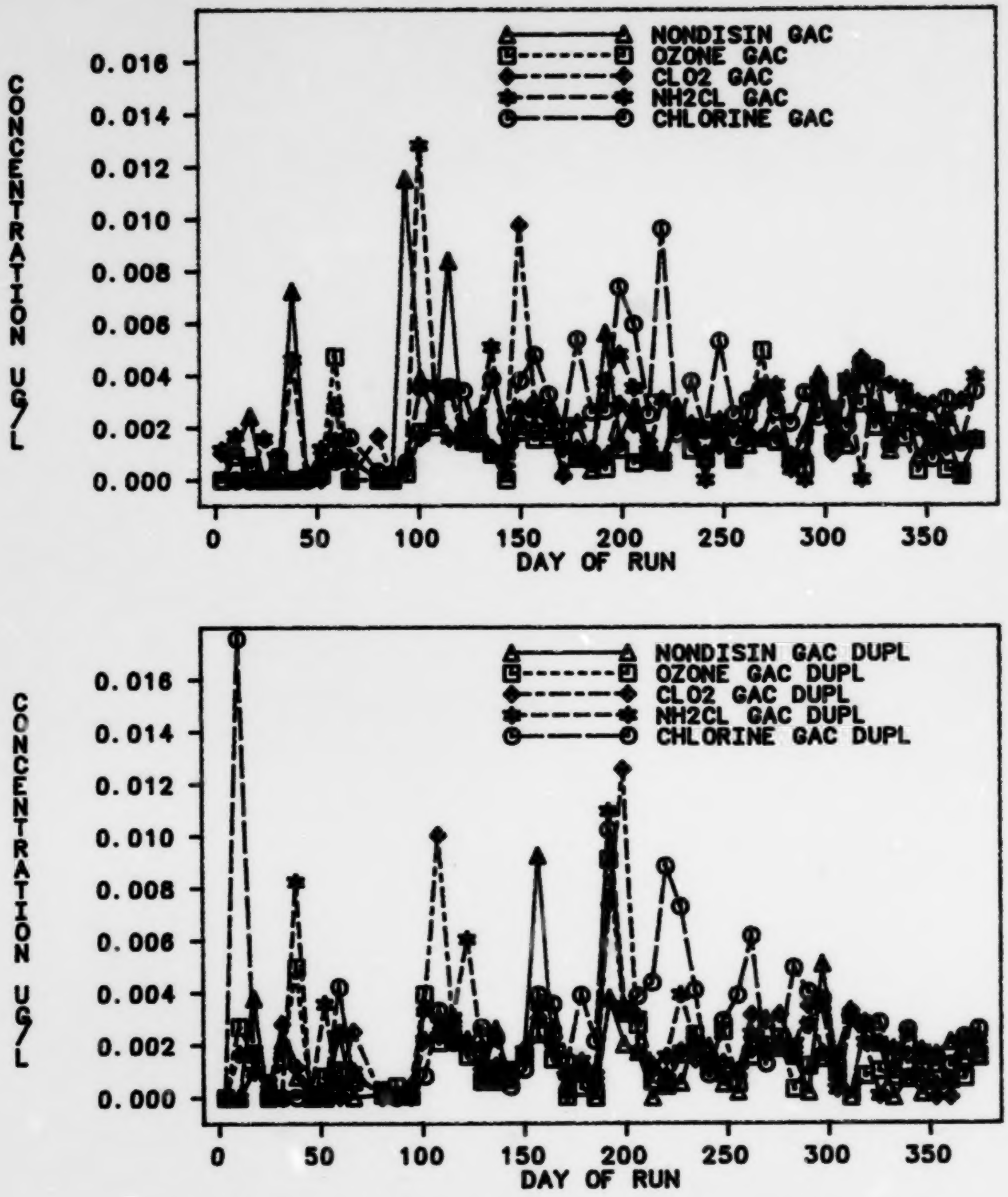


Figure 117. Comparison of the Total Nitrobenzene GAC and GAC Duplicate Effluent Levels for each Process Stream.

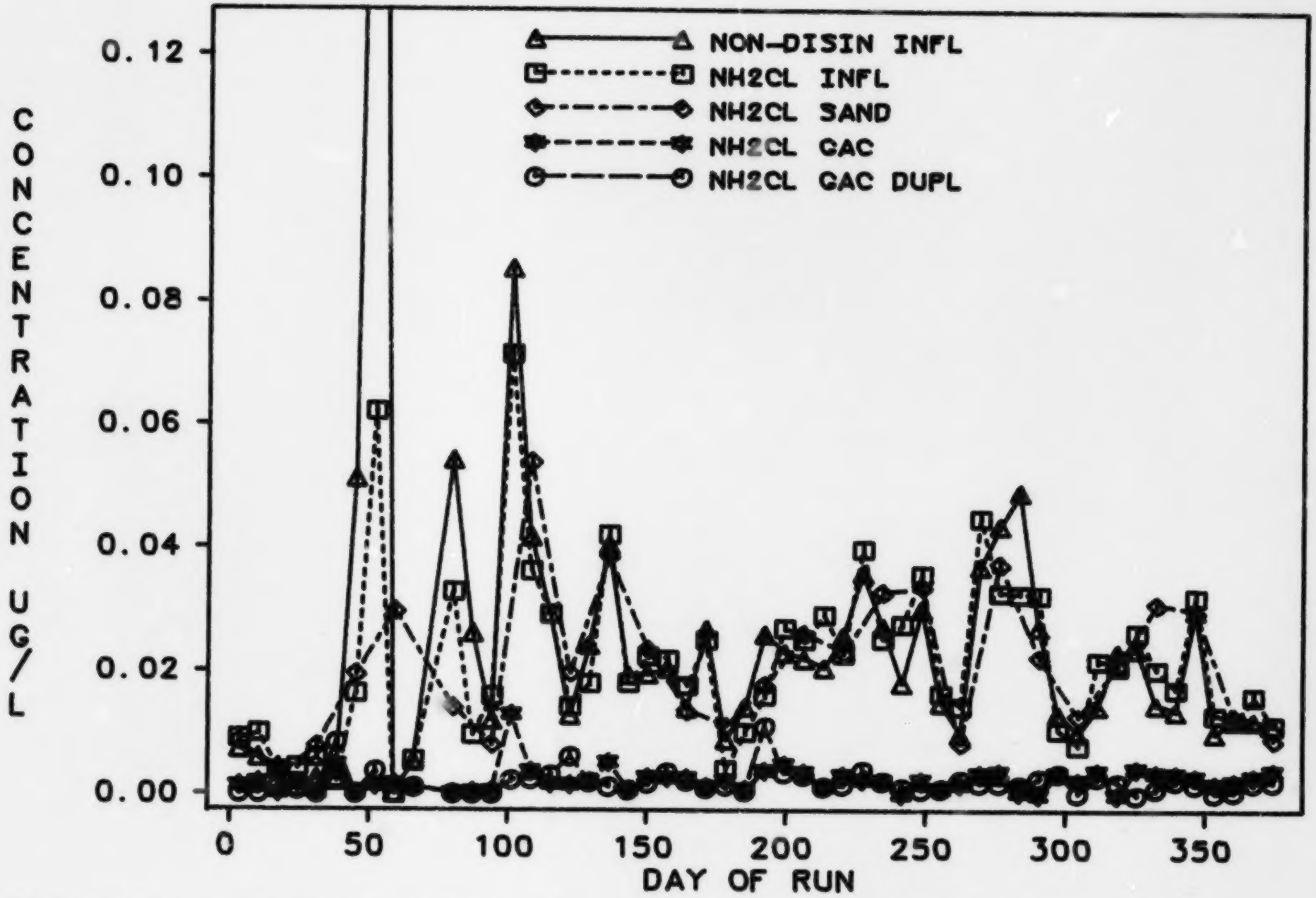


Figure 118. Total Nitrobenzene Breakthrough Profiles for the Chloramine Process Stream.

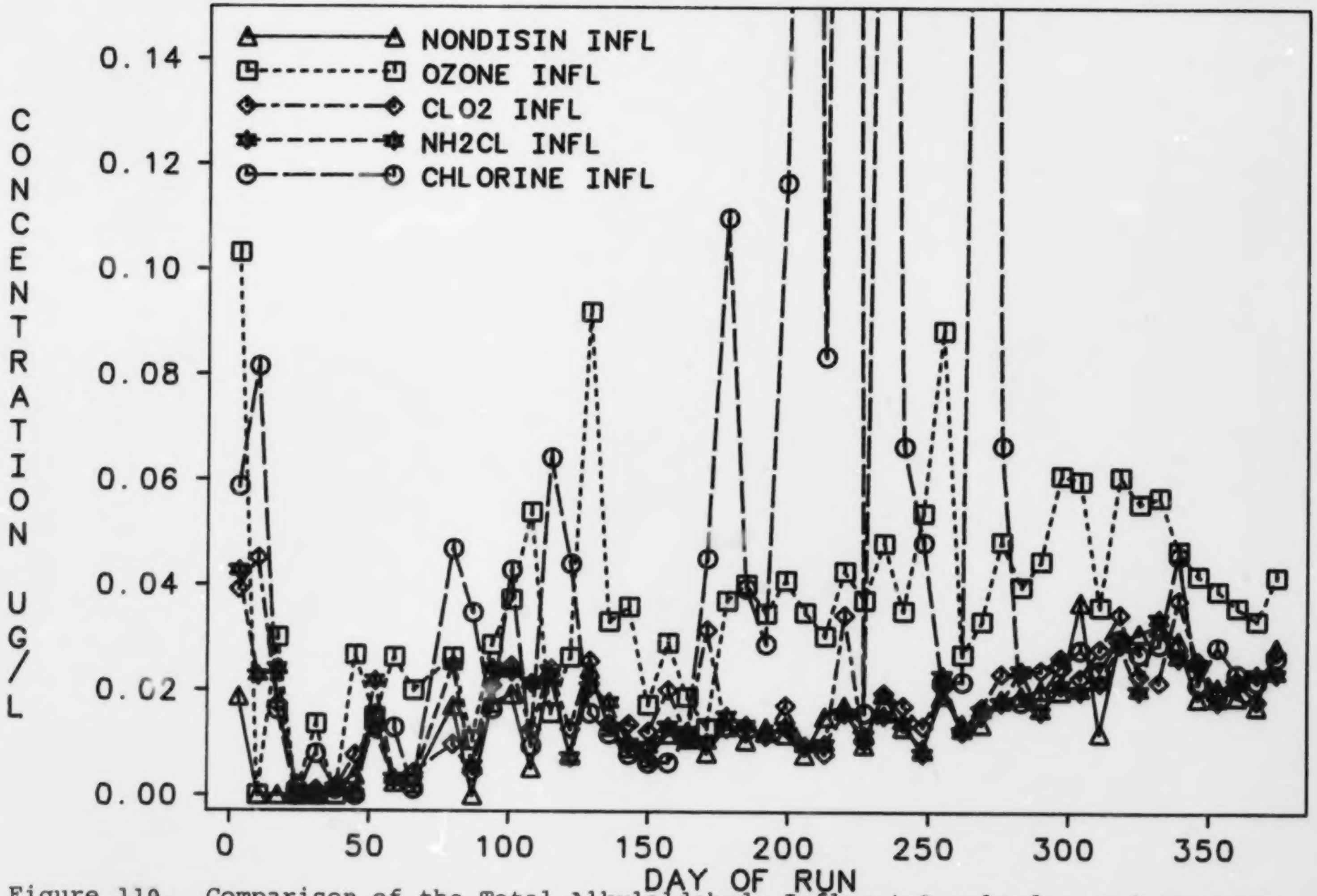


Figure 119. Comparison of the Total Alkylaldehyde Influent Levels for each Process Stream.

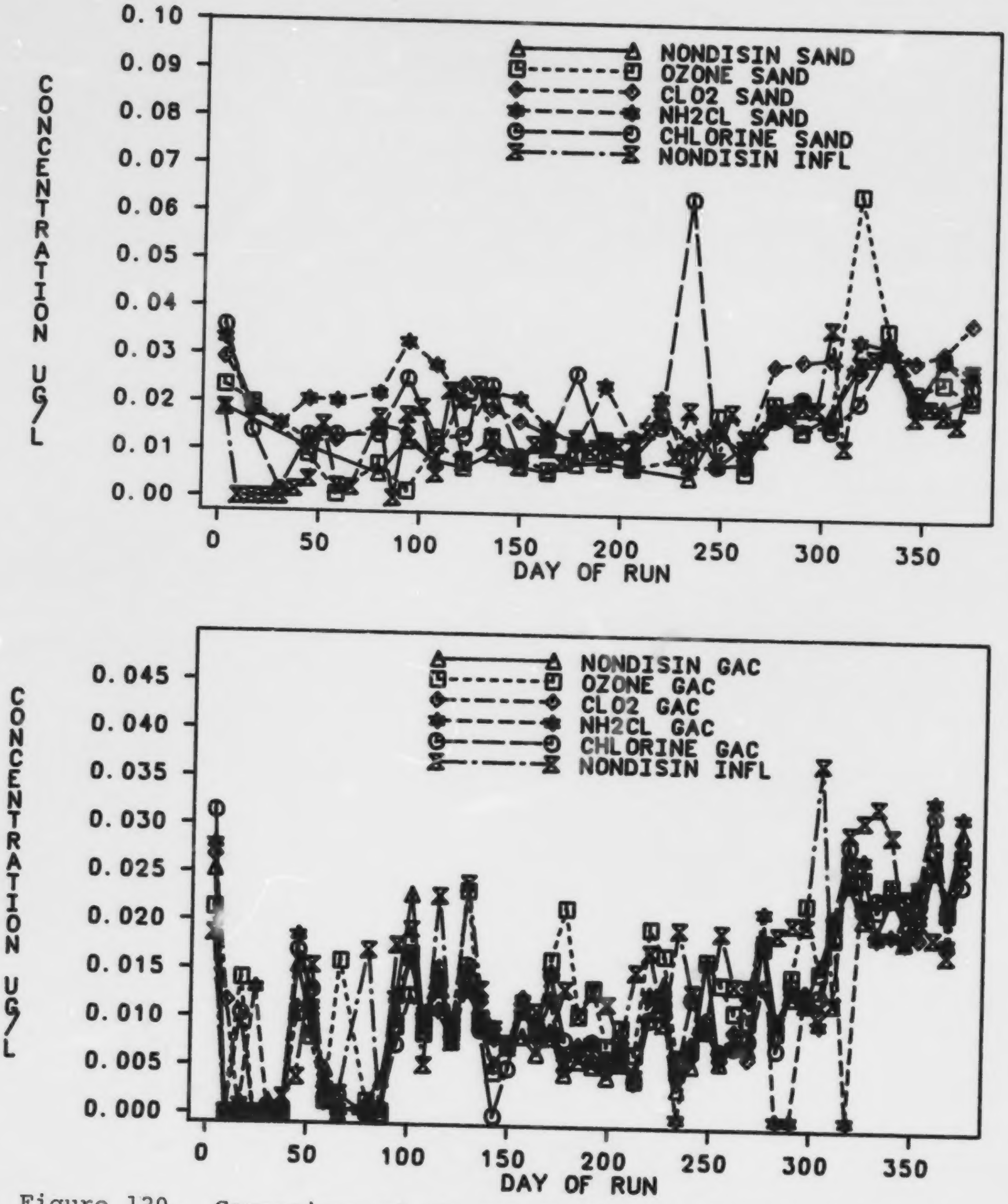


Figure 120. Comparison of the Total Alkylaldehyde Sand and GAC Effluent Levels for each Process Stream.

GAC columns of each process stream in the lower portion of this same figure.

OTHER SEMIVOLATILE ORGANICS

Several other semivolatile organics which do not belong to the aforementioned catagories were monitored during the operational period. These were tributylphosphate, triphenyl-methane, 4-nonylphenol, and d-fenchone. Although triphenylmethane was not confirmed by GC/MS analysis, the substance which eluted at the same GC retention time was quantitated as triphenylmethane and reported as such.

The frequency of occurrance of tributylphosphate in the nondisinfected influent was 98% with minimum, average, and maximum detected concentrations of 9.4, 40.7, and 158 ng/l, respectively. An average reduction of 89% was observed for ozonation while there were no effects observed for the other disinfectants. Similiarly, no reductions were observed across the sand columns of any of the process streams. The nondisinfected GAC and GAC duplicate columns exhibited average reductions of 92 and 95% while those of the other process streams ranged from 96 - 98%. Typical reductions of tributylphosphate are shown for the ozone process stream in Figure 121.

Triphenylmethane occurred in the nondisinfected influent at a frequency of 92% with minimum, average, and maximum detected concentrations of 0.83, 3.3, and 21.4 ng/l, respectively. A 38% average reduction was observed for 30 minutes of contact time with ozone while similiar contact with free chlorine produced an average reduction of 25%. The influent levels of triphenylmethane were uneffected by chlorine dioxide and chloramine. Additional removal was observed across the ozone sand column totaling 53% with respect to the nondisinfected influent. No removal across the sand columns of the other process streams were observed. Average removals ranging from 52 - 65% were observed across the GAC and GAC duplicate columns of all of the process streams. Although the average removals of the GAC columns fluctuated somewhat due to the erratic nature of the data, the removals relative to the nondisinfected influent were essentially equivalent for all of the GAC columns of the pilot column system. Typical reductions of triphenylmethane are shown for the chlorine dioxide system in Figure 122. While minimal removals were observed at lower concentrations, removals were considerably better when large concentration increases occurred.

The frequency of occurrence of 4-nonylphenol in the nondisinfected influent was 87% with minimum, average, and maximum detected concentrations of 5.2, 59.5, and 207 ng/l, respectively. Reductions were observed for all disinfectants

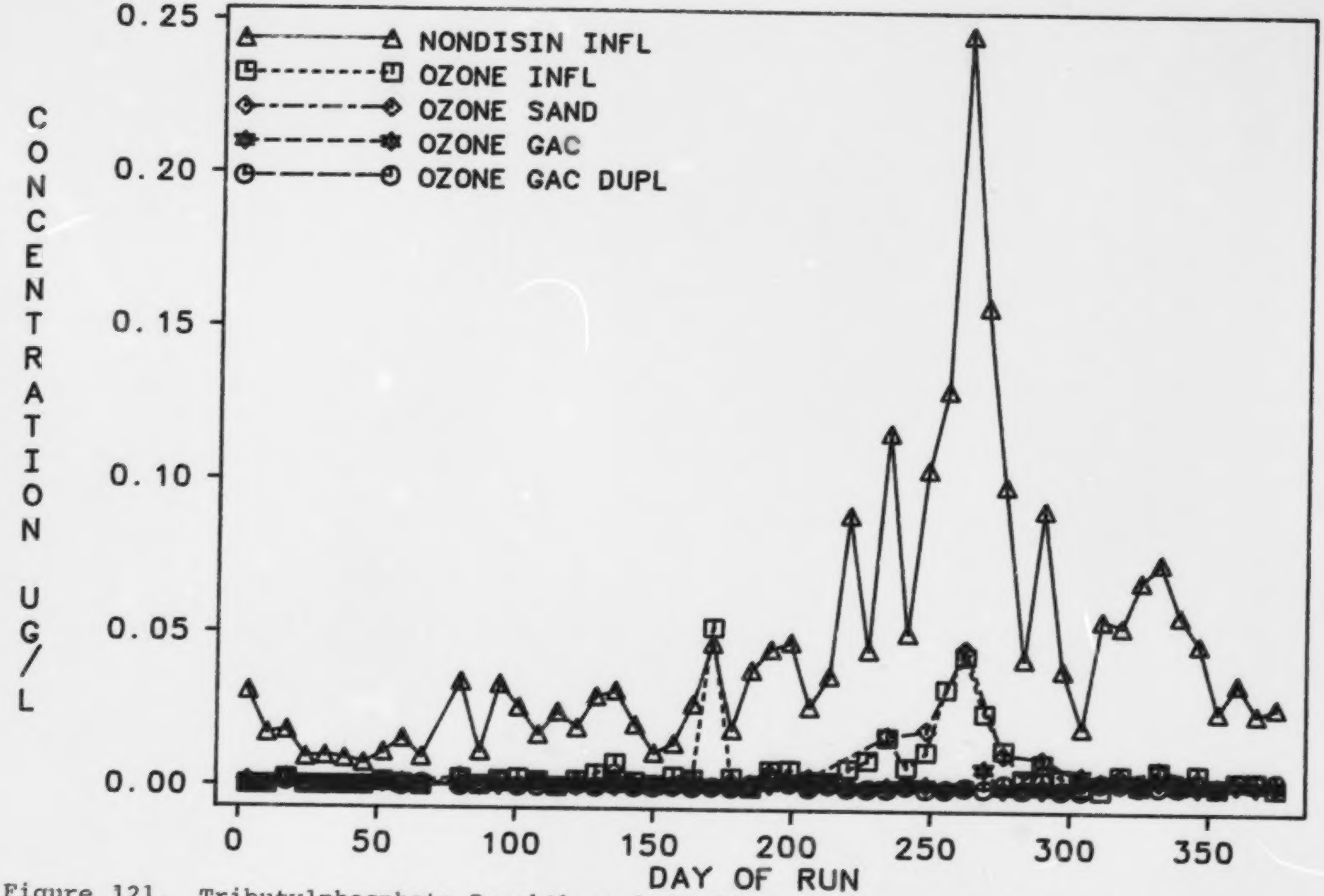


Figure 121. Tributylphosphate Breakthrough Profiles for the Ozone Process Stream.

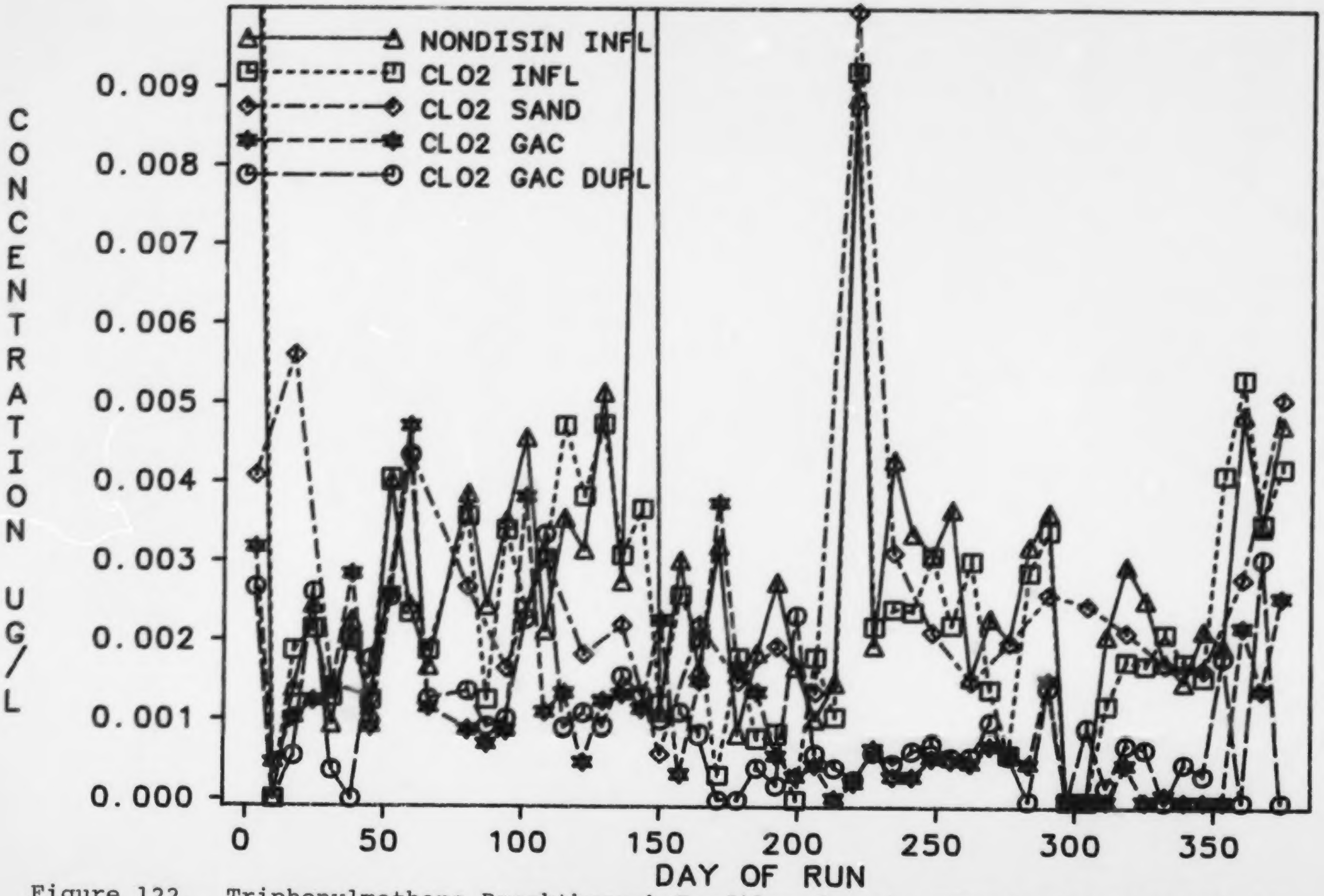


Figure 122. Triphenylmethane Breakthrough Profiles for the Chlorine Dioxide Process Stream.

with average removals of 72% for ozone, 54% for chlorine, 46% for chlorine dioxide, and 19% for chloramine. An additional removal averaging 42% with respect to the nondisinfected influent was observed across the chloramine sand column while an average removal of 33% was observed across the nondisinfected sand column. No additional removal was observed across the sand columns of the other disinfected process streams. Average removals ranging from 74 - 82% with respect to the nondisinfected influent were observed across the GAC and GAC duplicate columns of each process stream. Essentially all of the removal observed in the ozone process stream was attributable to ozonation with essentially no additional removal resulting from GAC filtration. Although the average removals of the GAC columns varied somewhat, their effluent concentrations were essentially the same for each process stream. Typical removals of 4-nonylphenol are indicated in Figure 123 for the chlorine process stream.

The frequency of occurrance of d-fenchone in the nondisinfected influent was 77% with minimum, average, and maximum detected concentrations of 0.36, 5.6, and 17.7 ng/l, respectively. An average reduction of 59% was observed for ozonation while chlorination produced an increase of approximately 133% as indicated in Figure 124. While an average reduction of 40% occurred across the chlorine sand column relative to the chlorine influent, the reduction with respect to the nondisinfected influent was essentially zero. No reductions were observed across the sand columns of the other process streams. The removals of d-fenchone with respect to the nondisinfected influent across the GAC and GAC duplicate columns of the nondisinfected, ozone, chloramine, and chlorine process streams were essentially equivalent. There average removals were varied somewhat ranging from 80 - 94% due to the erratic nature of the data below 1 ng/l. The average removals observed for the GAC and GAC duplicate columns of the chlorine dioxide process stream, however, were somewhat lower at 58% and 64%, respectively. The effluent concentration profiles of these GAC columns, which are depicted in Figure 125, suggest that saturation occurred around day 320 at the 7 ng/l level. These effluent concentration profiles differed from those of the other process streams, which are typified in Figure 124, in that those of the other process streams did not reach a state of saturation.

DISINFECTION BY-PRODUCTS

As indicated in previous sections, TOX as well as several specific species of organic contaminants were observed to increase after 30 minutes of disinfectant contact time with the various disinfectants under evaluation. Both chlorinated and nonchlorinated by-products were observed with the chlorinated by-products predominating. The primary by-products formed which

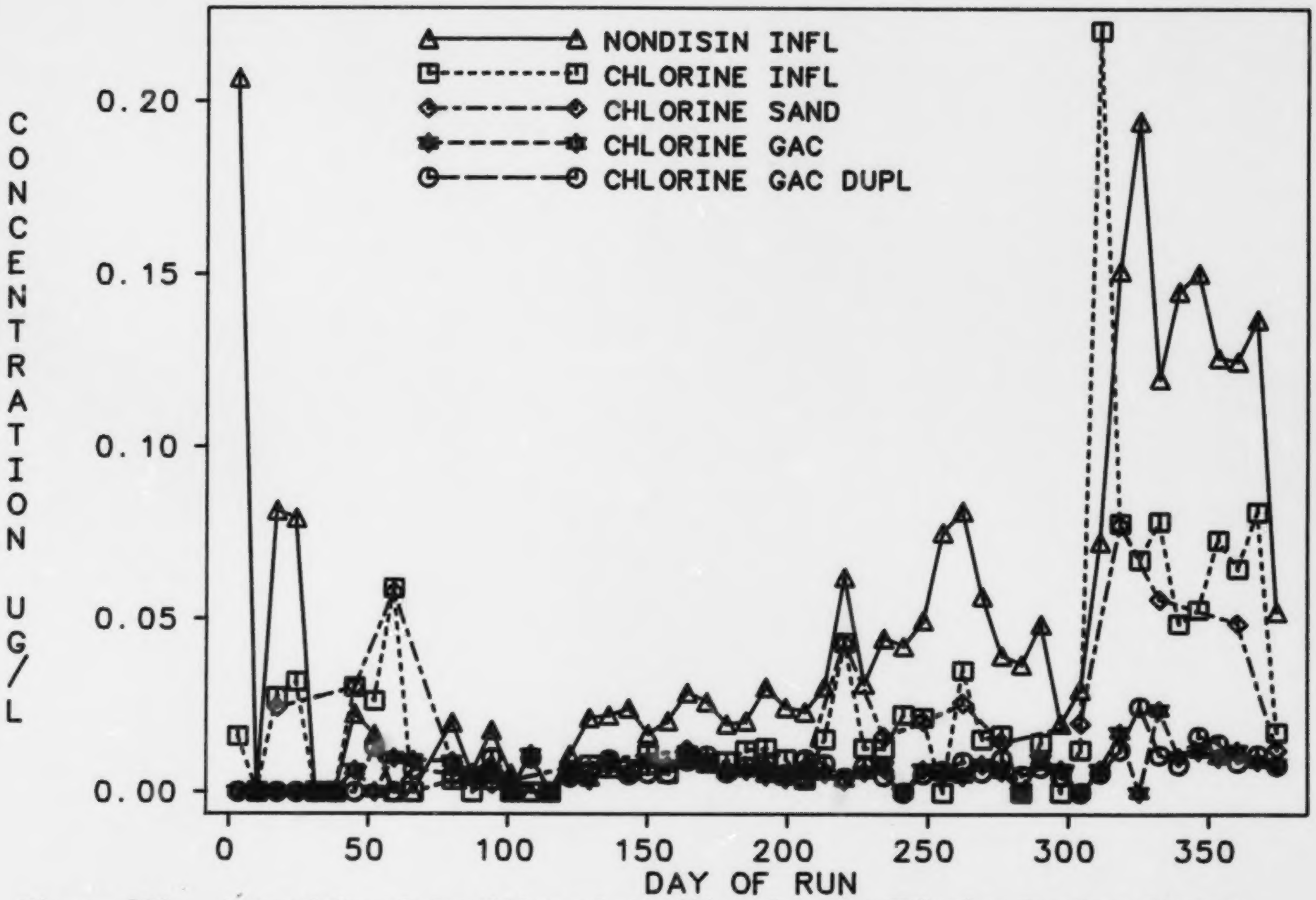


Figure 123. 4-Nonylphenol Breakthrough Profiles for the Chlorine Process Stream.

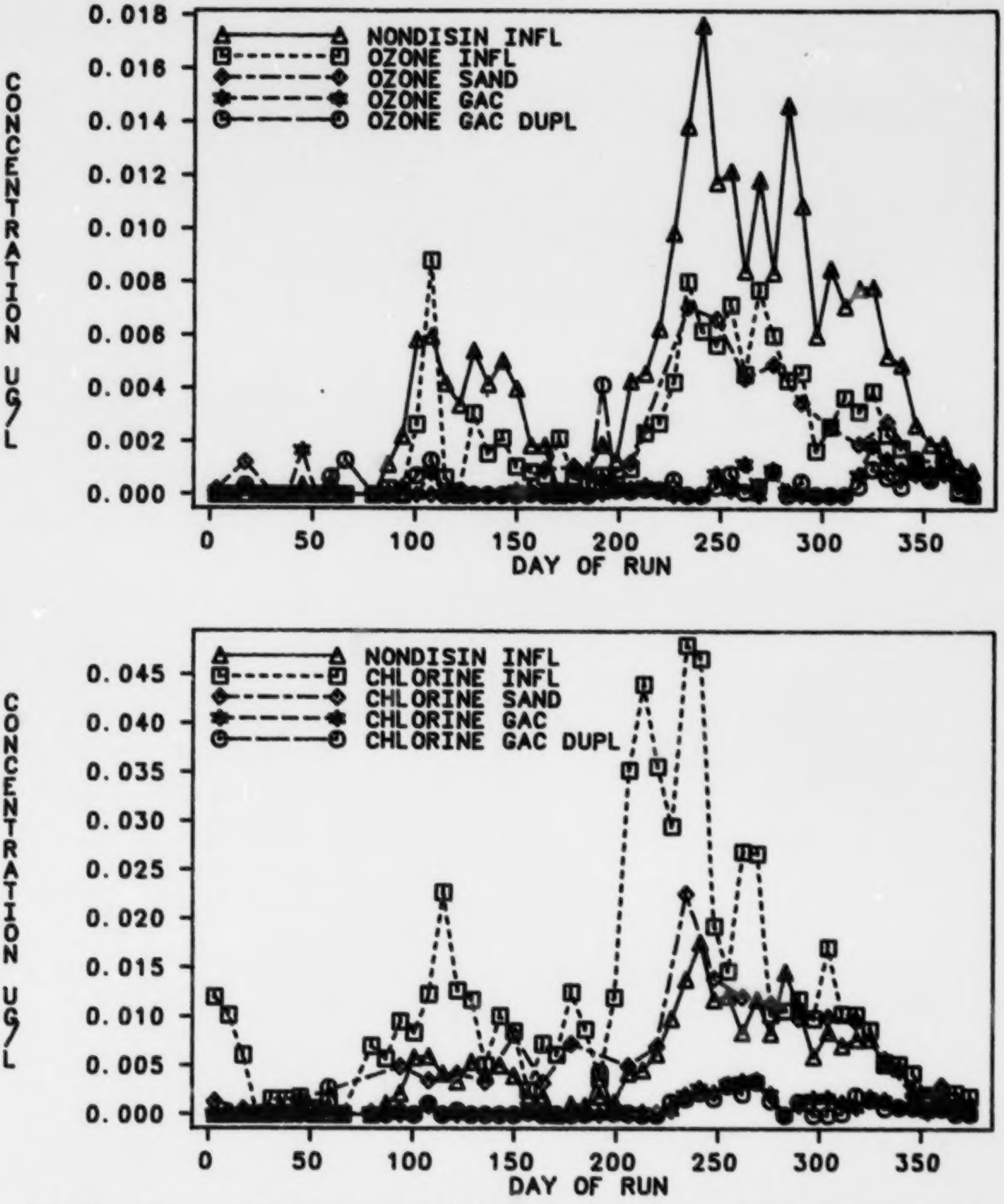


Figure 124. d-Fenchone Breakthrough Profiles for the Ozone and Chlorine Process Streams.

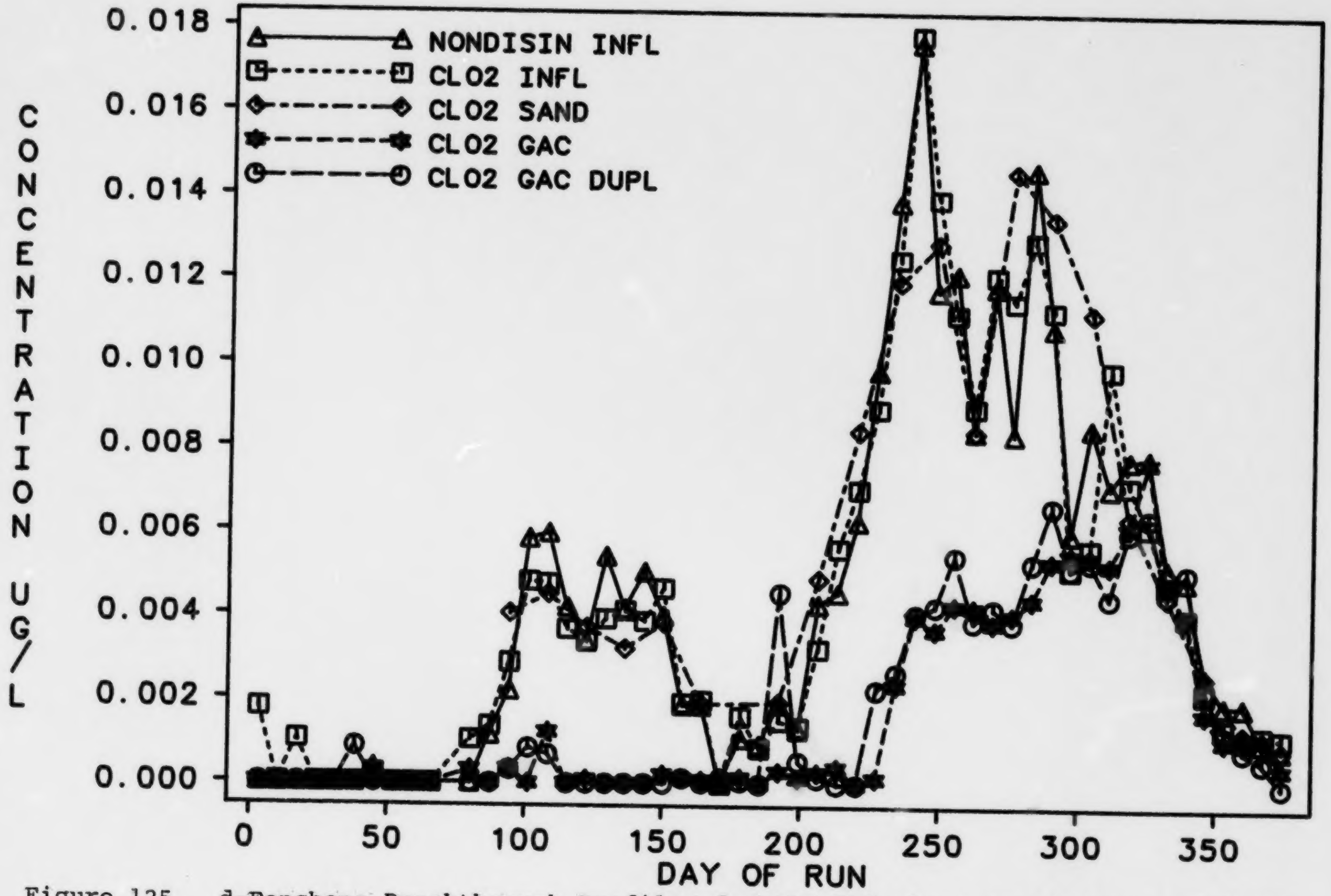


Figure 125. d-Fenchone Breakthrough Profiles for the Chlorine Dioxide Process Stream.

have been identified and confirmed by external standards were the trihalomethanes, chlorobenzenes, alkylbenzenes, and alkylaldehydes. The initial and final average concentrations of each of these individual substances formed by the various disinfectants after 30 minutes of disinfectant contact time are listed in Table 30. As indicated in earlier discussions on TOX and THMs, the formation of these constituents in the chloramine contact chamber is attributable to a brief 9 second contact with free chlorine resulting from a pulsed ammonia feed. It is estimated, based upon post operational period evaluations, that the final average concentrations of TOX and THMs could be reduced to 20 ug/l and 0 ug/l, respectively, using the proper technique for generating chloramines. It is also reasonable to assume that those semivolatile constituents indicated for the chloramine system would also be reduced accordingly since the majority of these substances are common to those found in the chlorine system.

Those semivolatile by-products listed in Table 30 in no way constitute all of the semivolatile by-products formed. This is particularly true for the chlorine system which contains numerous semivolatile by-products. The extent of semivolatile by-product formation for the influent of each disinfectant process stream can be observed in the flame ionization and electron capture GC profiles depicted in Figures 126 and 127, respectively. These profiles representing day 87 of the operational period have been normalized with respect to the area of the internal standard and are thus directly comparable with respect to intensity. A "cross" is indicated at the top of each internal standard peak. In general, the number and level of semivolatile by-products formed by the disinfected process streams as indicated in these figures were ozone < chlorine dioxide < chloramine <<< chlorine. However, when chloramines are properly produced without the presence of free chlorine, it is estimated that the level of semivolatile by-products formed in the chloramine process stream would be less than or equal to that of the chlorine dioxide system. Although variations occurred throughout the operational period, these relative relationships of the extent of by-product formation among the disinfectant process streams remained essentially unchanged.

Because of the difficulty involved in estimating the extent of by-product formation directly from chromatographic data, two parameters entitled total flame ionization and total electron capture concentration were created in order to evaluate the relative relationships of by-product formation among the disinfectants under study. The total flame ionization concentration (TFIC) was determined by subtracting the areas of the solvent front and those of the internal standards from the total chromatographic area followed by quantitation relative to the quantitation internal standard, 1-chlorododecane. The total

TABLE 30. PRIMARY BY-PRODUCTS IDENTIFIED IN THE INFLUENT OF EACH DISINFECTANT PROCESS STREAM AND CONFIRMED BY EXTERNAL STANDARDS.

	INITIAL AVERAGE CONC (ug/l)	FINAL AVERAGE CONC. (UG/L) AFTER 30 MINUTES OF DISINFECTANT CONTACT TIME			
	NONDISIN	OZONE	CHLORINE DIOXIDE	CHLOR-AMINE	CHLORINE
TOX	25	--	85	117*	263
TOTAL THM's	1.3	--	--	4.5*	34
ALKYLBENZENES:					
1,2,4,5-tetramethyl-benzene	0.004	--	0.007	--	0.031
1,2,3,4-tetramethyl-benzene	0.004	--	--	--	0.056
2,ethyltoluene	0.004	--	--	--	0.016
3-ethyltoluene	0.010	--	--	--	0.014
4-ethyltoluene	0.010	--	--	0.016*	0.016
1,3-diethyl-benzene	0.003	--	0.010	--	0.005
1,4-diethyl-benzene	0.002	--	0.005	--	0.005
p-cymene	0.002	--	--	0.006*	0.132
CHLOROBENZENES:					
1,2-dichloro-benzene	0.008	--	--	--	0.010
1,3-dichloro-benzene	0.002	--	--	--	0.051
1,4-dichloro-benzene	0.009	--	--	--	0.017
1,2,4-trichloro-benzene	0.006	--	--	--	0.062
ALKYLALDEHYDES:					
octanal	0.005	0.014	--	--	0.062
nonanal	0.013	0.028	--	--	0.014
d-fenchone	0.006	--	--	--	0.013

---

* By-products formed by brief contact with free chlorine

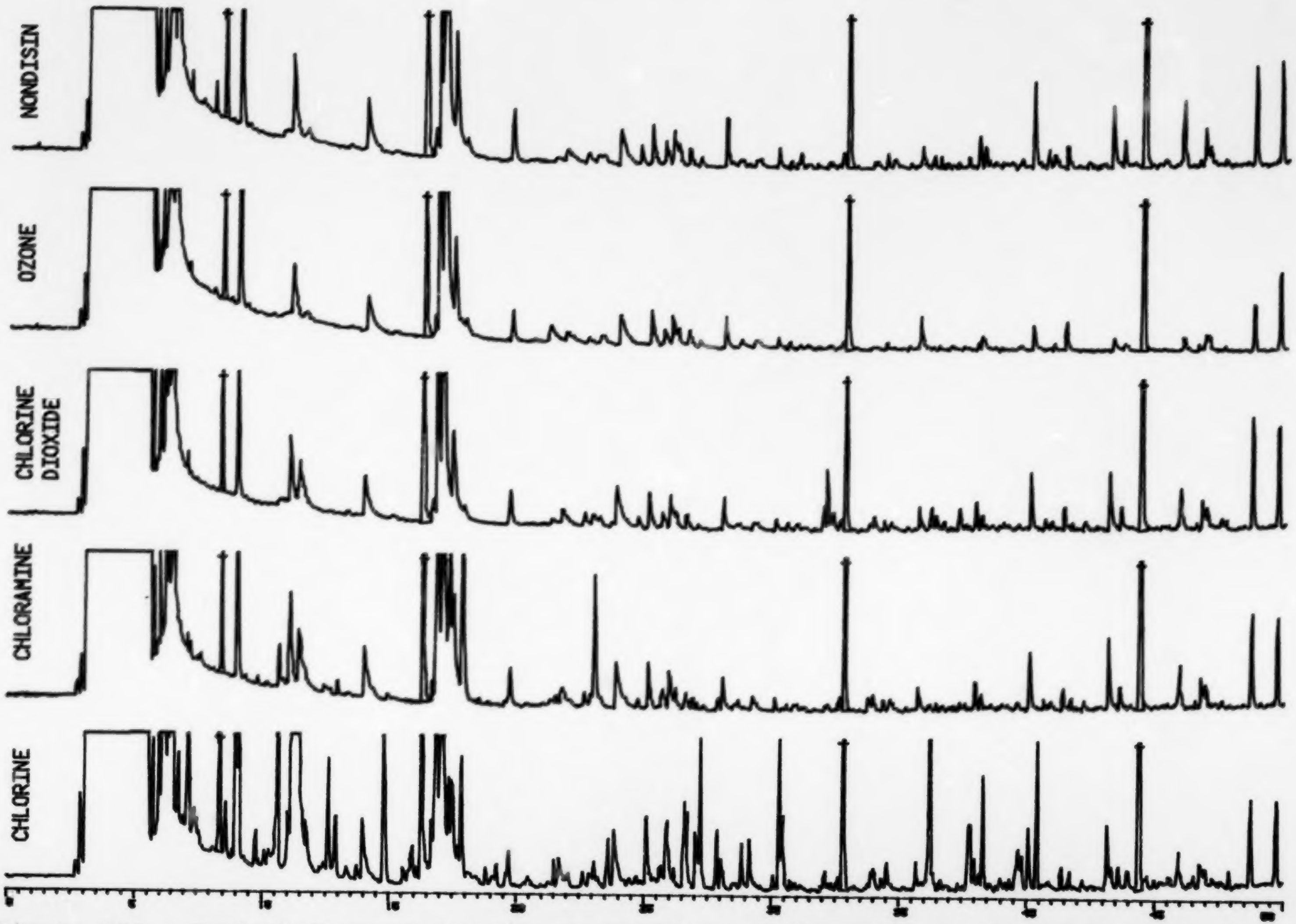


Figure 126. Typical Flame Ionization GC Profiles of the Influent Locations of each Process Stream Obtained on Day 87.

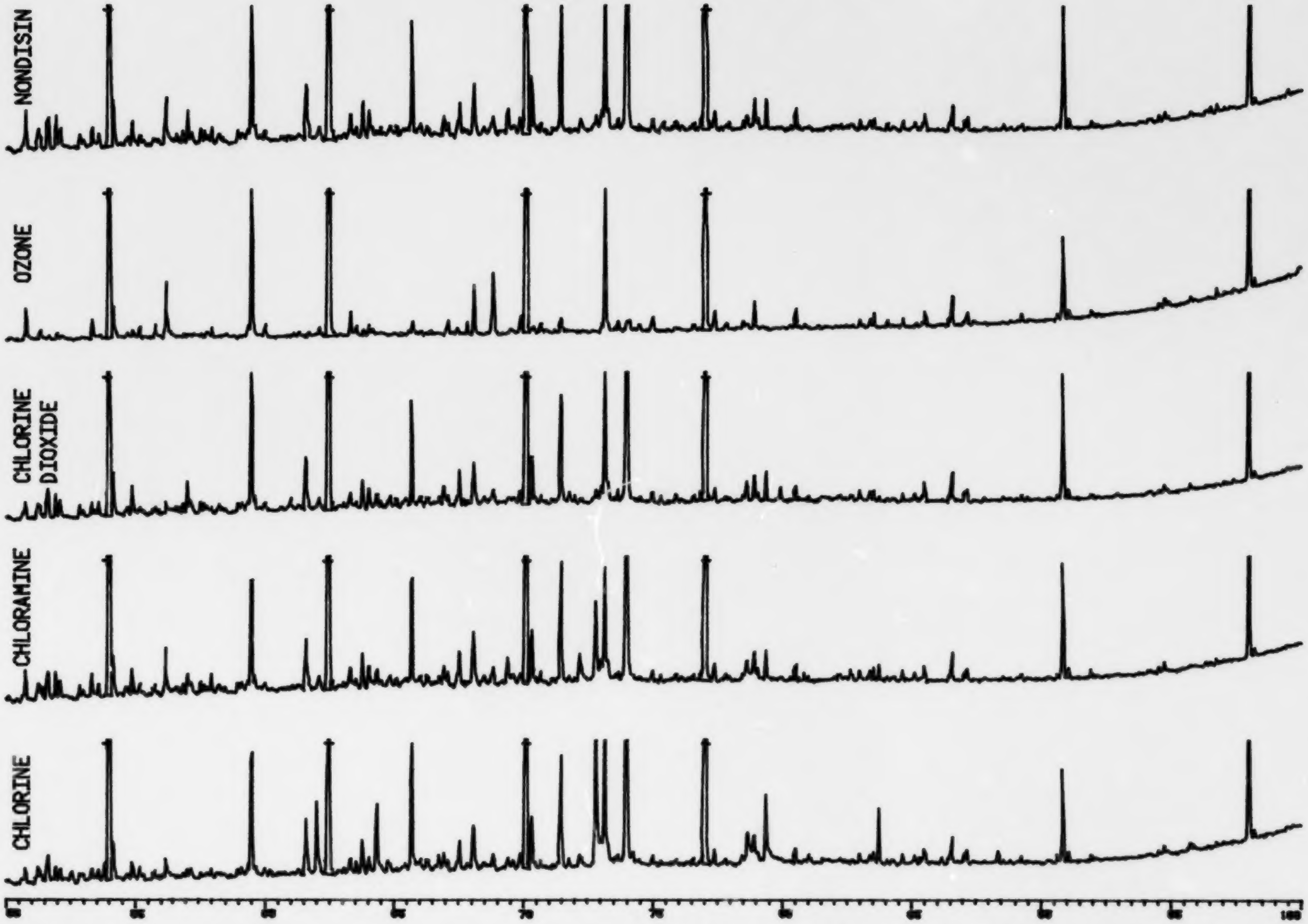


Figure 126. (Cont.) Typical Flame Ionization GC Profiles of the Influent Locations of each Process Stream Obtained on Day 87.

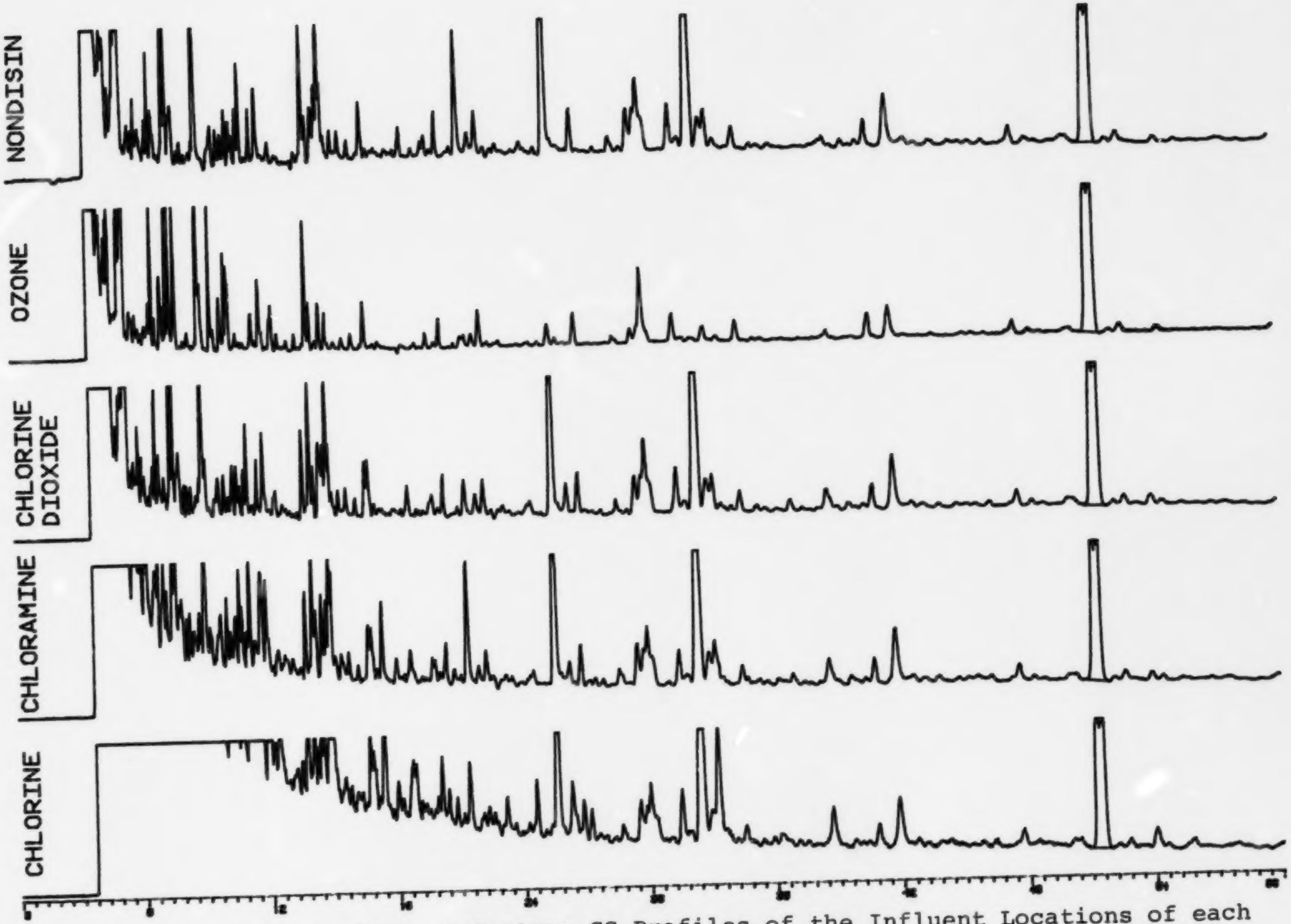


Figure 127. Typical Electron Capture GC Profiles of the Influent Locations of each Process Stream Obtained on Day 87.

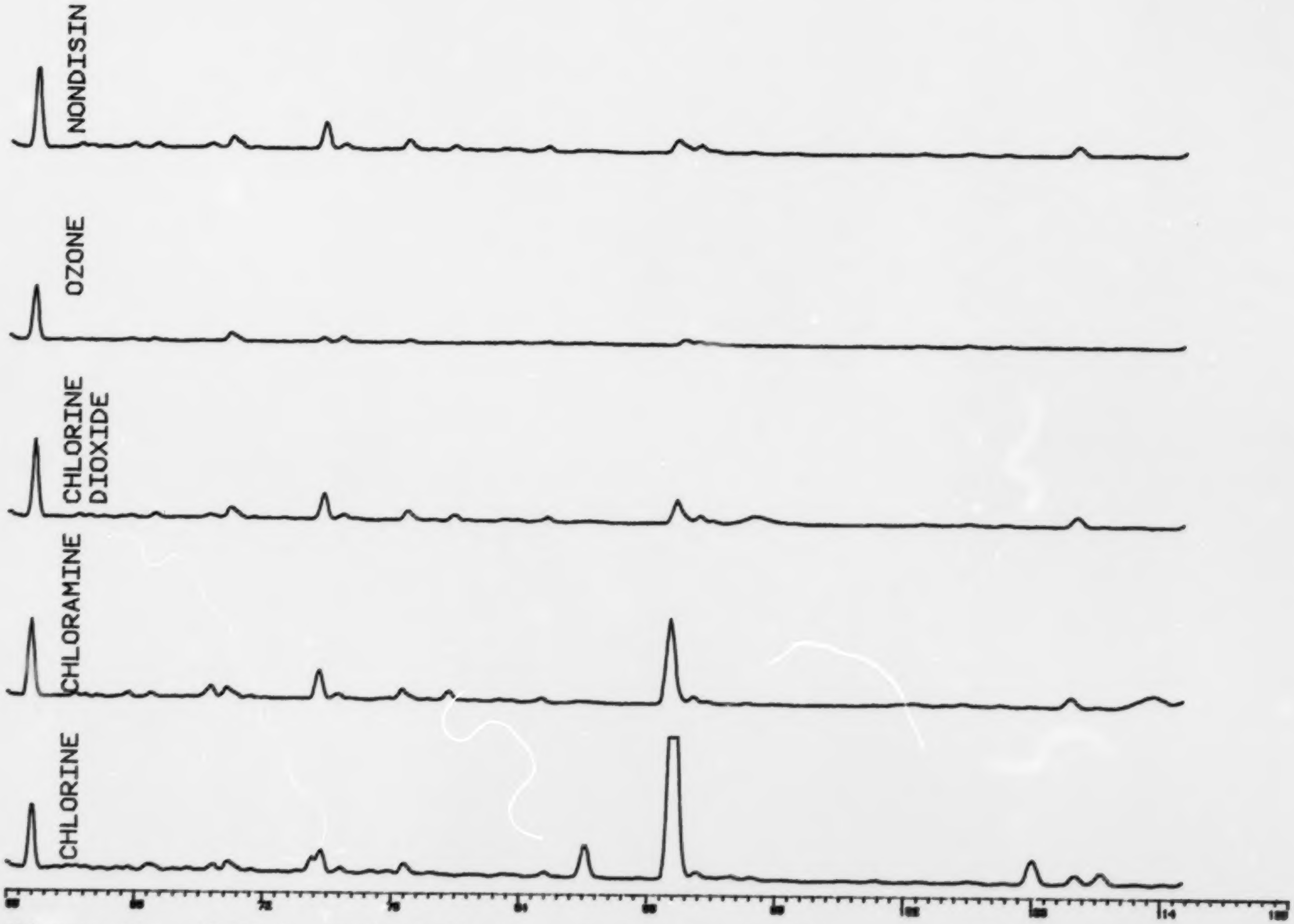


Figure 127. (Cont.) Typical Electron Capture GC Profiles of the Influent Locations of each Process Stream Obtained on Day 87.

electron capture concentration (TECC) was quantitated in a similiar fashion except that no solvent front area was subtracted since pentane and hexane are nonresponsive to the electron capture detector, and that the internal standard used for quantitation was endosulfan I. Unfortunately, these two parameters were not monitored until day 157 of the operational period. A comparison of the total flame ionization concentration in the influent for each process stream is presented in Figure 128 while that of the total electron capture concentration is presented in Figure 129. Relative to the nondisinfected influent whose average TFIC was 3.9 ug/l as 1-chlorododecane, ozonation produced an average reduction of 41% while the TFIC of the nondisinfected influent was essentially uneffected by chlorine dioxide. On the other hand, an average increase in TFIC of 17% was observed for chloramine while a 245% increase was observed for chlorine. Relative to an average nondisinfected influent TECC of 0.38 ug/l, ozonation produced an average reduction of 40% while average increases of 11, 165, and 495% were produced by 30 minutes of disinfectant contact time with chlorine dioxide, chloramine, and chlorine, respectively. Again it should be mentioned that the TECC of the chloramine influent would be considerably reduced when generating chloramines without the presence of free chlorine.

The flame ionization and electron capture GC profiles of the sand column effluents of each process stream for day 87 of the operational period are compared in Figures 130 and 131. Comparison of these profiles to those of their respective influents in Figures 126 and 127 indicated that many of the organic substances present were reduced somewhat across the sand columns of the various process streams. These reductions can be more easily observed by comparing the TFIC and the TECC for the sand effluents of the various process streams in Figures 132 and 133 with those of their respective influents which were previously presented in Figures 128 and 129. The greatest reduction in TFIC, averaging 41% was observed across the chlorine sand column with an average influent concentration of 18.3 ug/l as 1-chlorododecane and average sand effluent concentration of 8.6 ug/l. This average effluent TFIC, however, still represents an average increase of 98% with respect to the nondisinfected influent. The second greatest reduction in TFIC, averaging 32% was observed across the nondisinfected sand column with an average influent concentration of 3.9 ug/l and an average effluent concentration of 2.4 ug/l. The average ozone influent TFIC was reduced an additional 6% across the ozone sand column. For a total average reduction of 47% with respect to the nondisinfected influent. Sand filtration in the chlorine dioxide system resulted in a 10% average reduction in TFIC with respect to the nondisinfected influent while an average increase of 6% was observed across the chloramine sand column for an overall average increase of 25% with respect to the nondisinfected

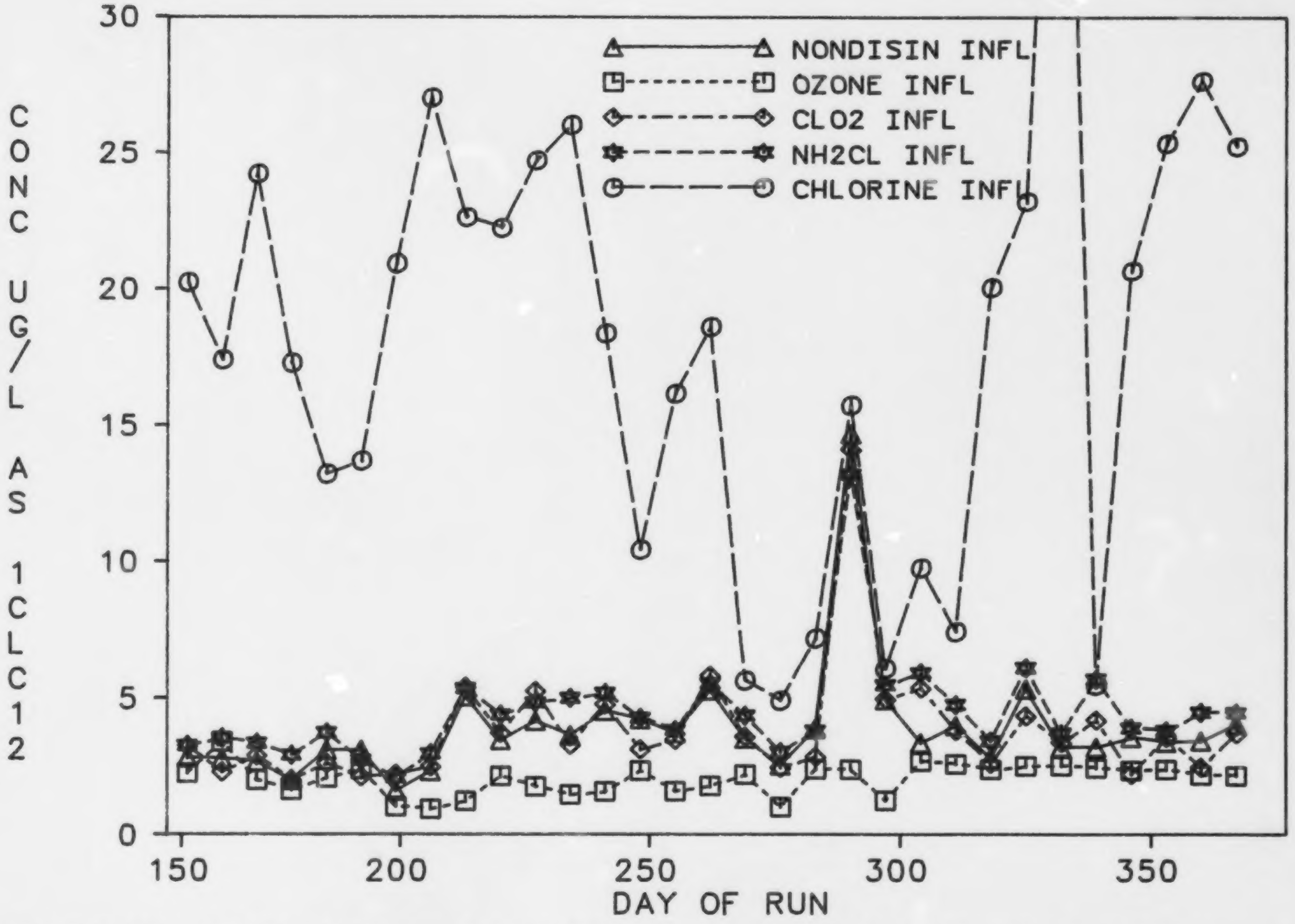


Figure 128. Total Flame Ionization Concentrations in the Influent of each Process Stream.

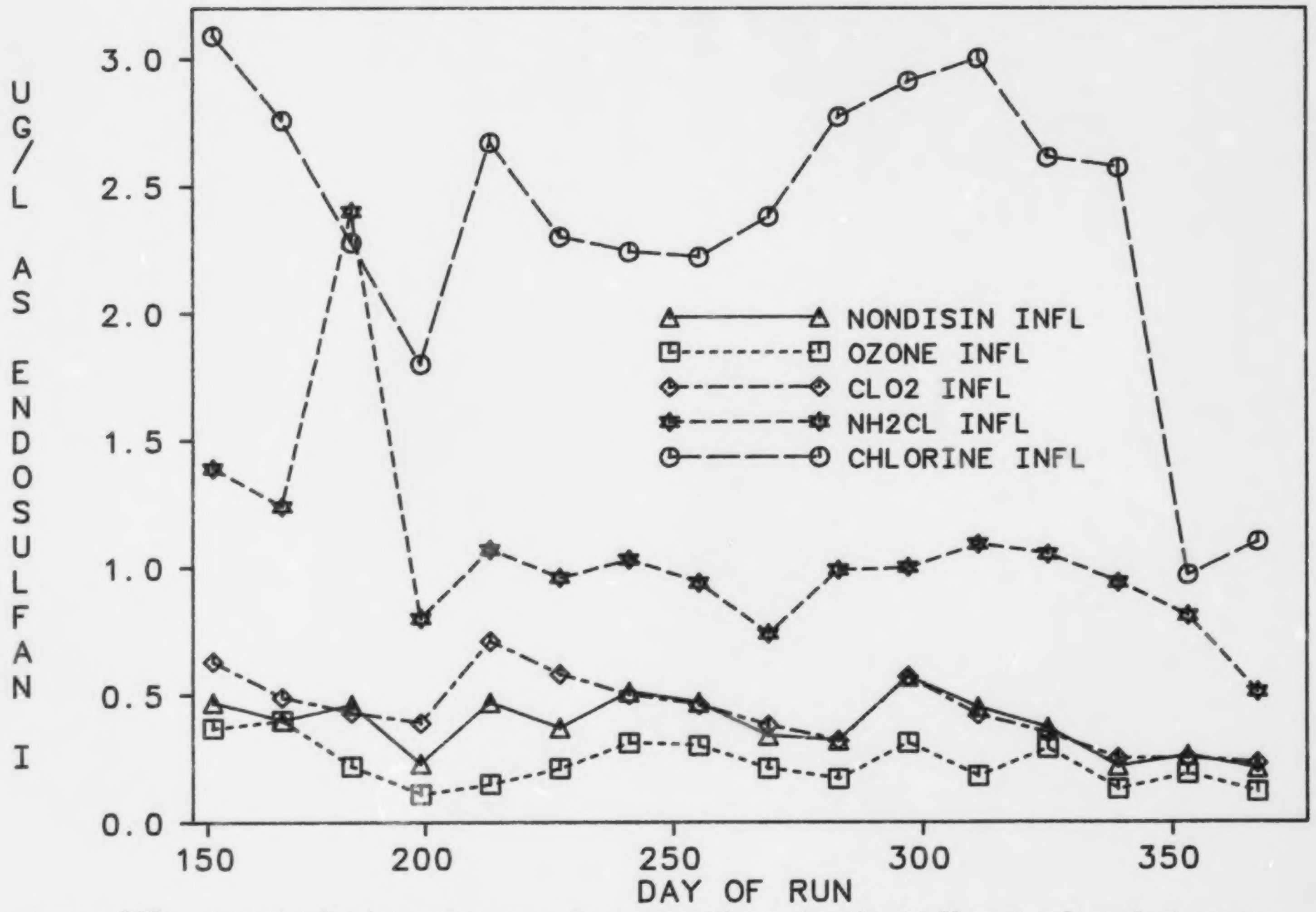


Figure 129. Total Electron Capture Concentrations in the Influent of each Process Stream.

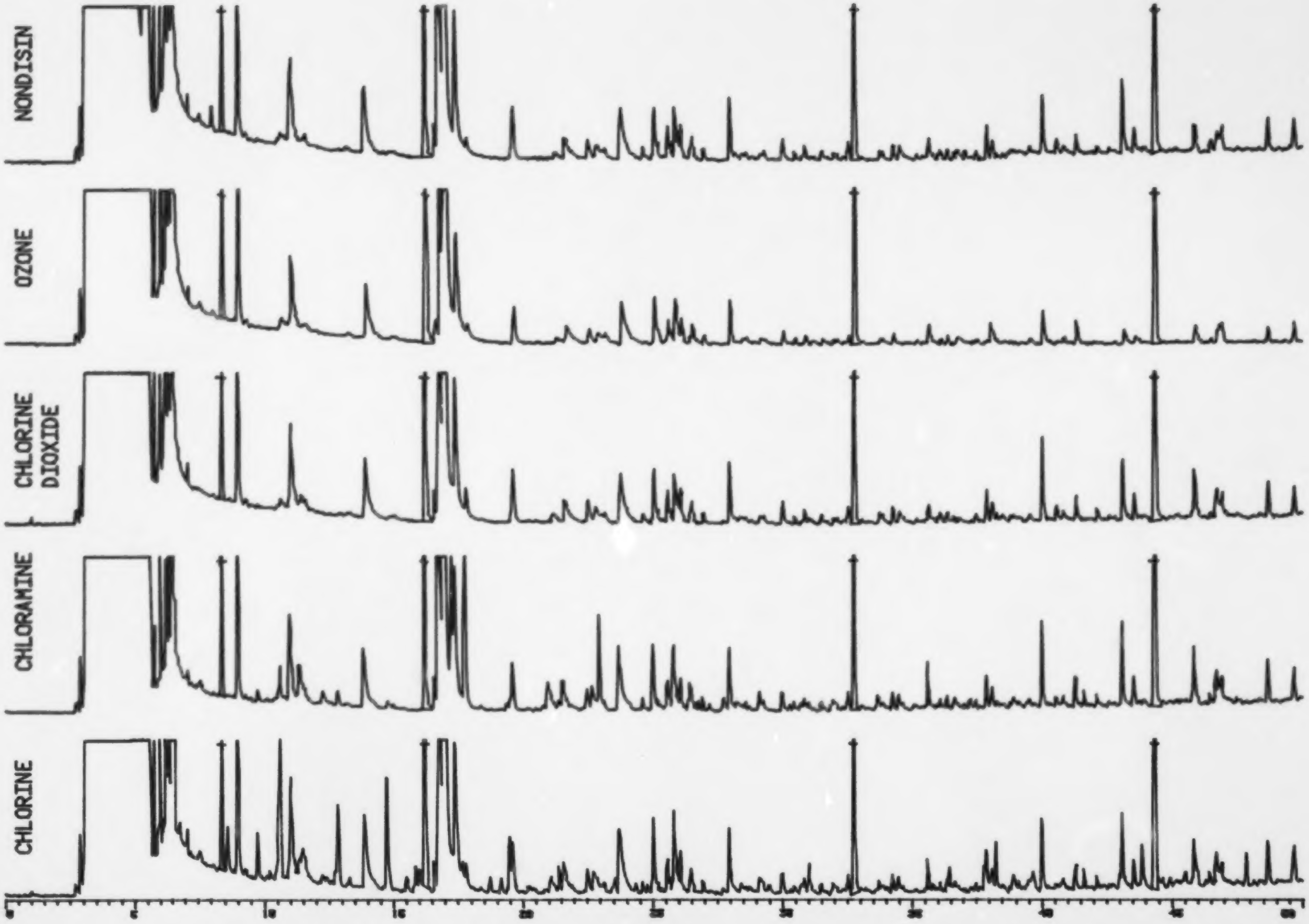


Figure 130. Typical Flame Ionization GC Profiles of the Sand Column Effluent of each Process Stream Obtained on day 87.

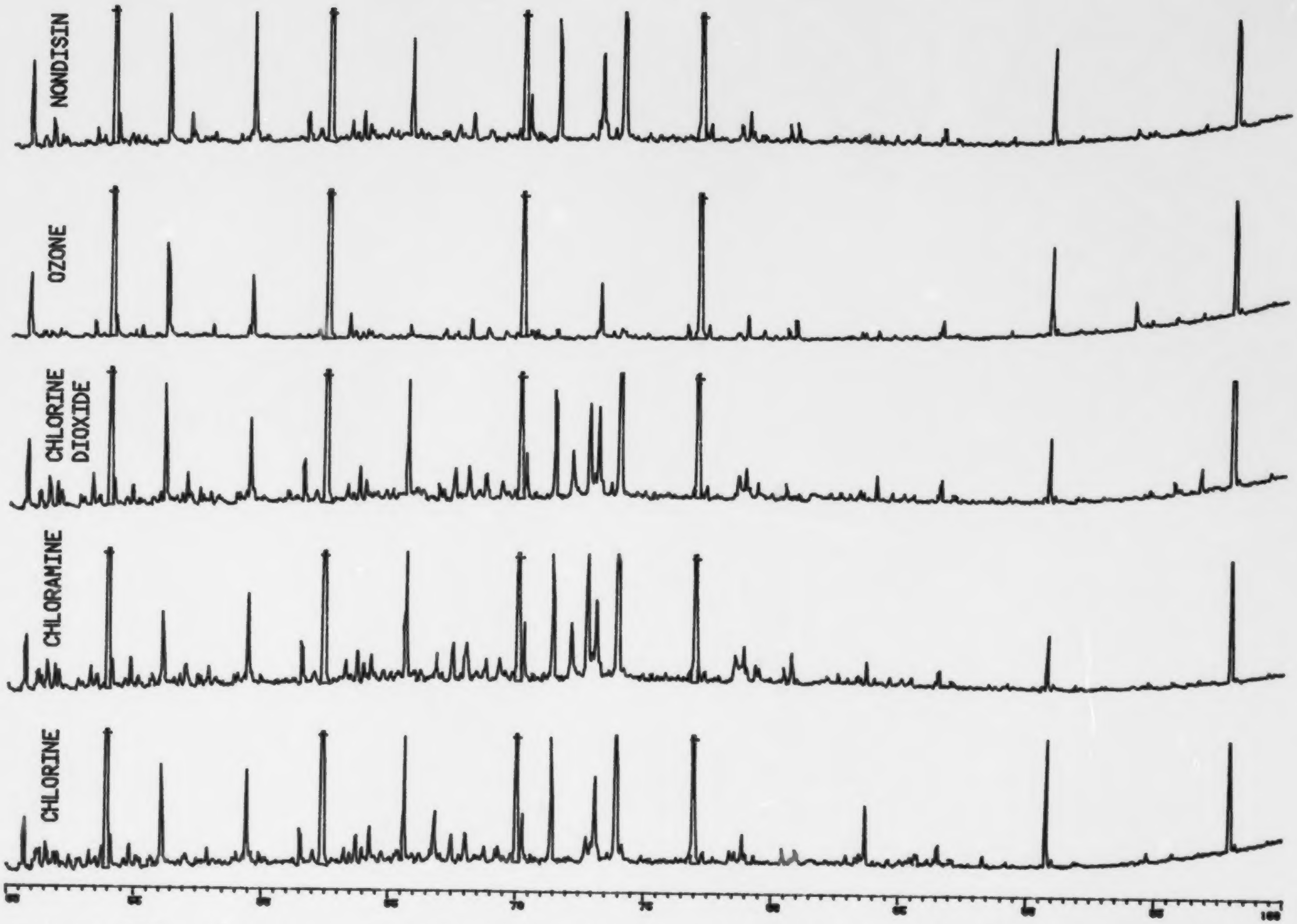


Figure 130. (Cont.) Typical Flame Ionization GC Profiles of the Sand Column Effluent of each Process Stream Obtained on Day 87.

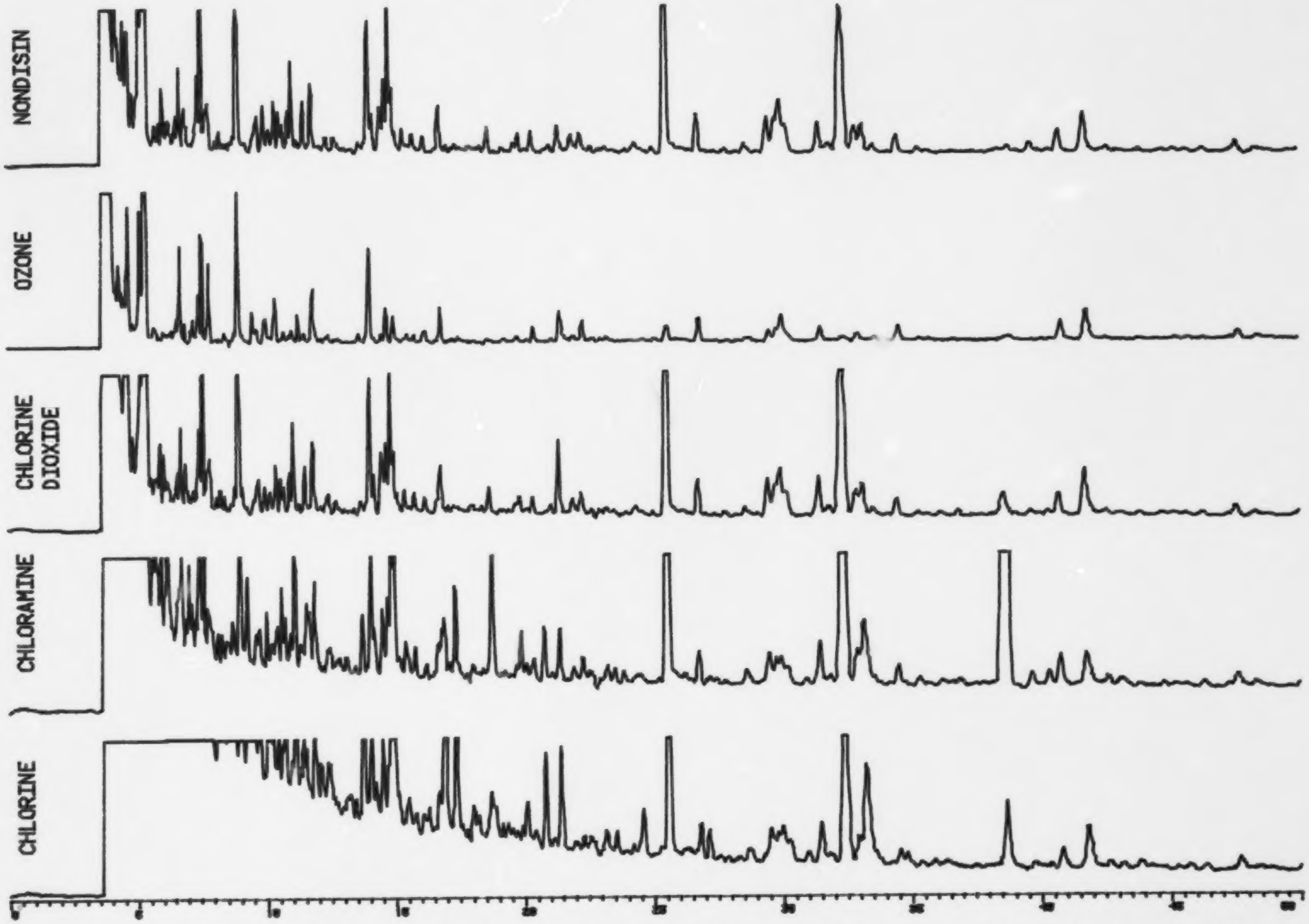


Figure 131. Typical Electron Capture GC Profiles of the Sand Column Effluent of each Process Stream Obtained on Day 87.

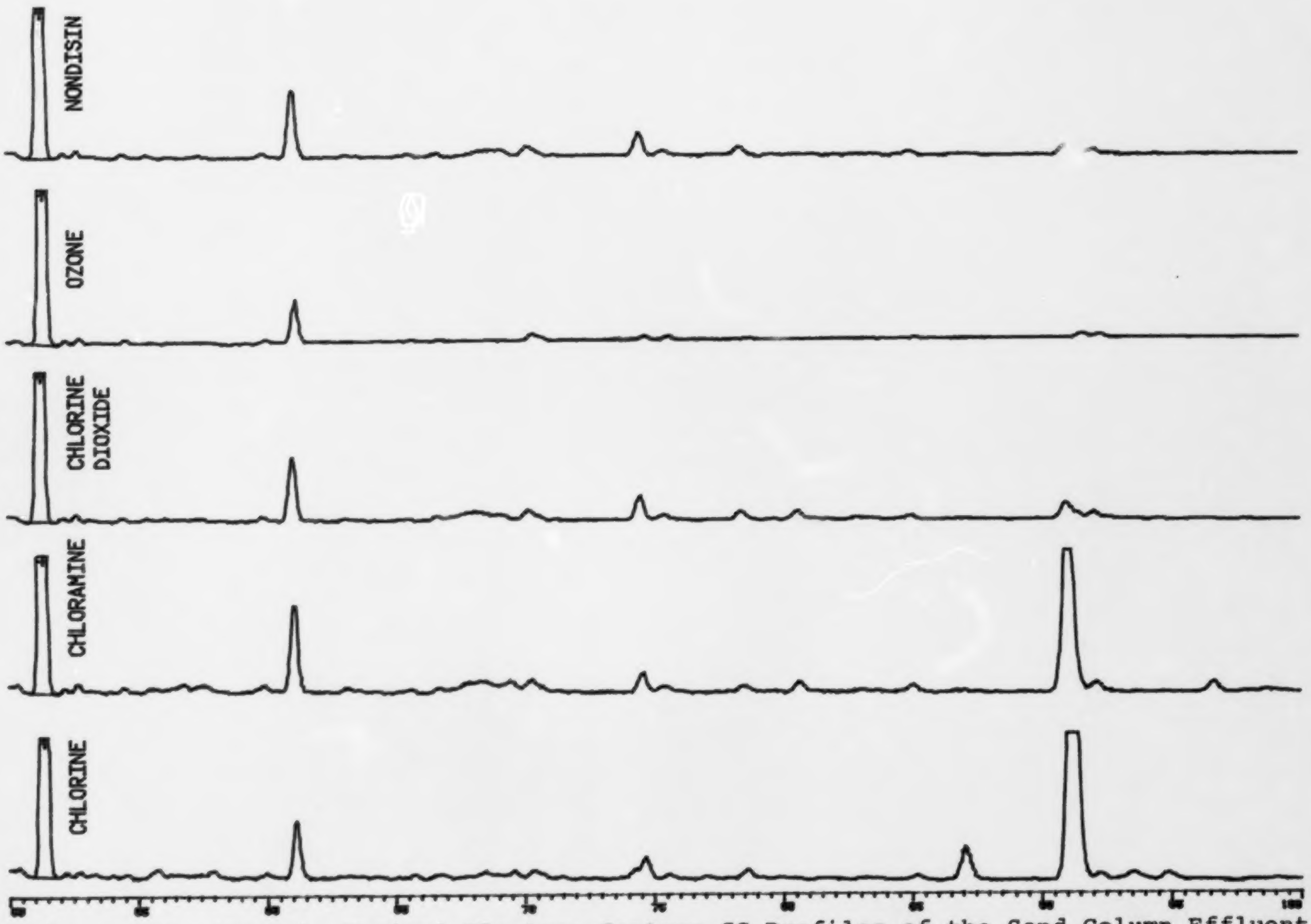


Figure 131. (Cont.) Typical Electron Capture GC Profiles of the Sand Column Effluent of each Process Stream Obtained on Day 87.

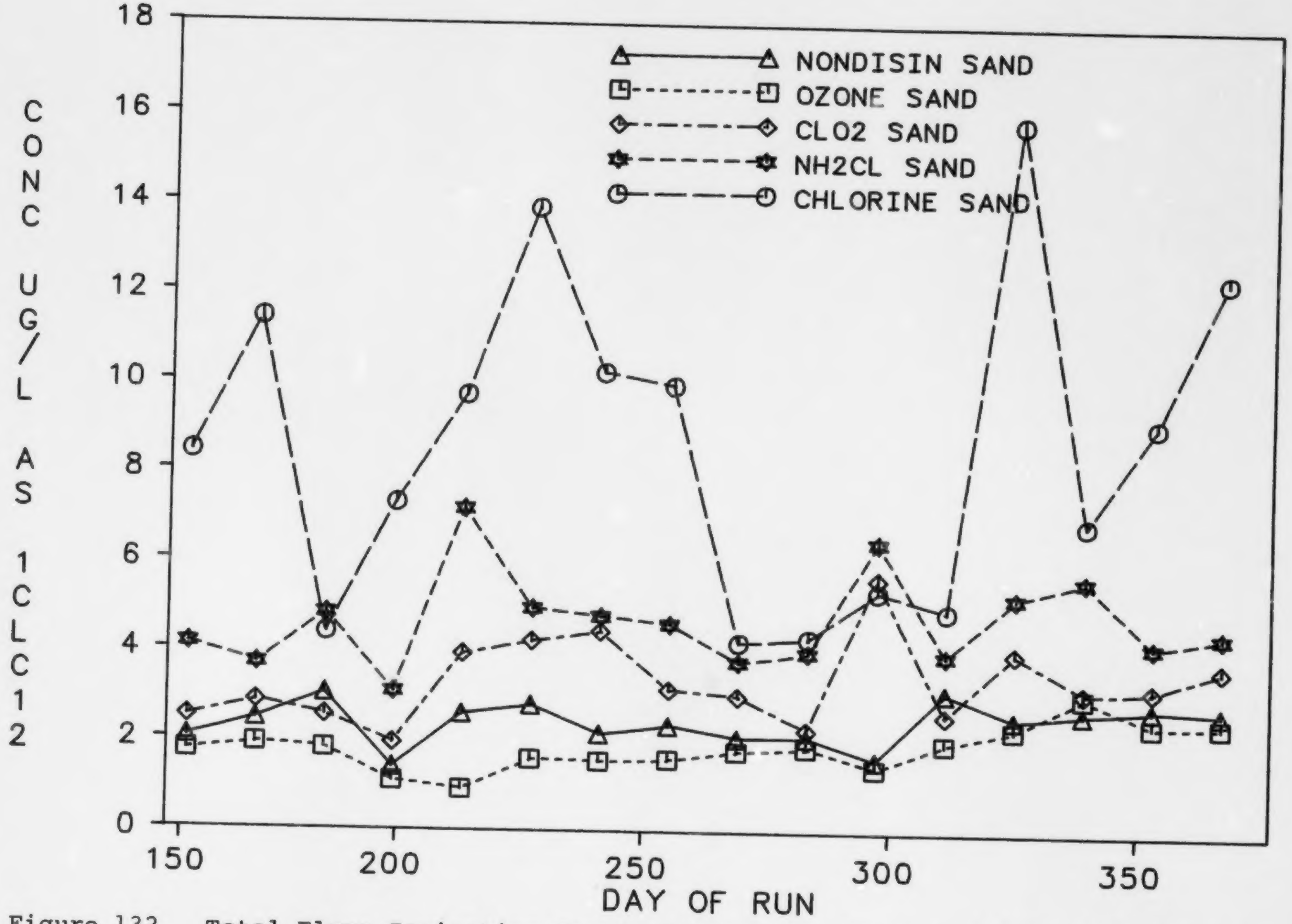


Figure 132. Total Flame Ionization Concentrations in the Sand Column Effluent of each Process Stream.

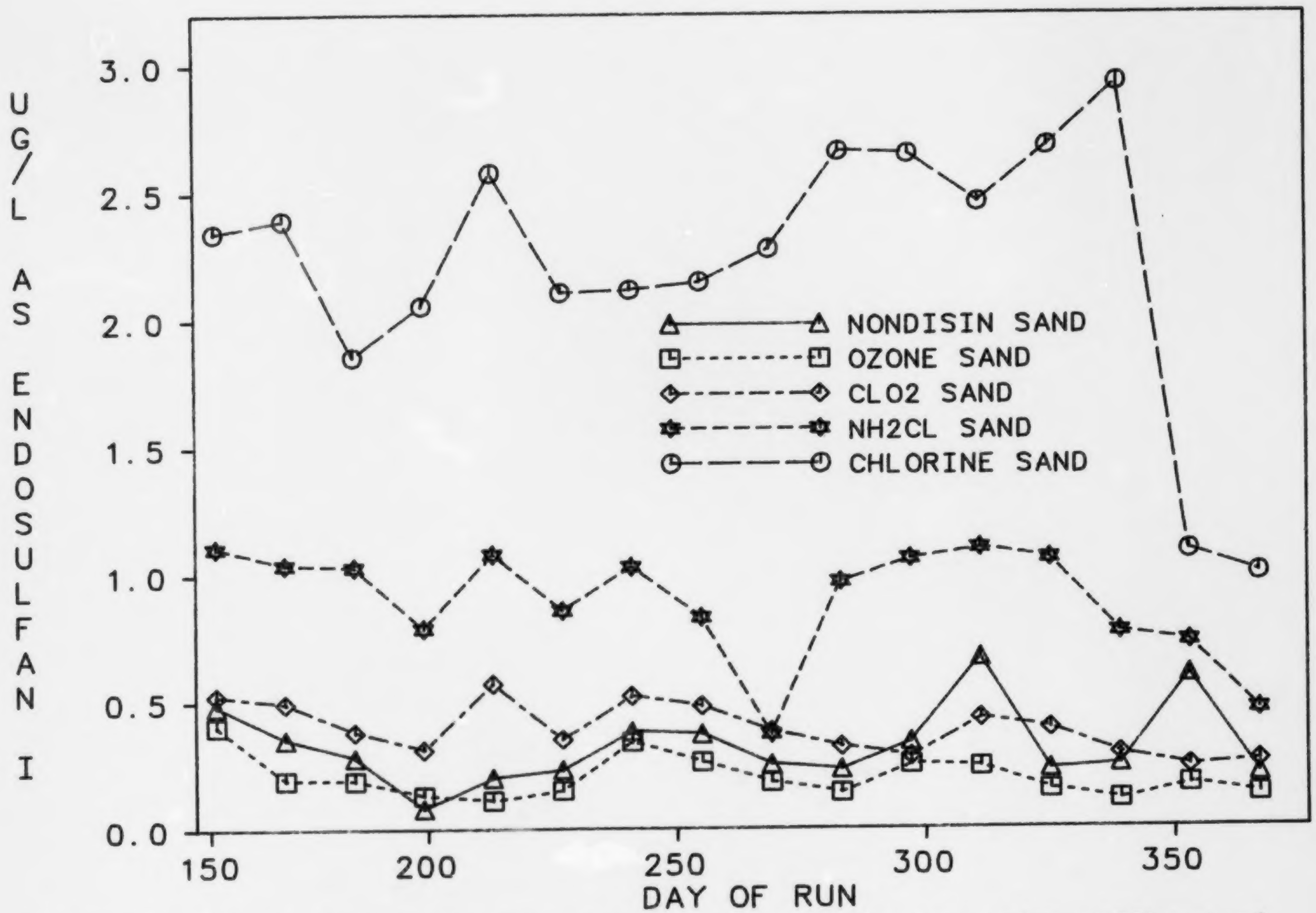


Figure 133. Total Electron Capture Concentrations in the Sand Column Effluent of each Process Stream.

influent. Similiarly, relative to the TECC in the nondisinfected influent, the TECC in the effluent of the nondisinfected sand column was reduced an average of 12% while the average reduction observed in the ozone process stream increased from 40% for ozonation to 48% across the ozone sand column. There were essentially no reductions observed in TECC across the sand column of the chlorine dioxide process stream. Slight average reductions in TECC were observed across the sand columns of the chloramine and chlorine process streams. However, the TECC in the effluent of these sand columns remained, respectively, 125% and 456% higher than that of the nondisinfected influent.

The effects of GAC filtration on the removal of semivolatile organic substances including disinfection by-products during each quarter of the one year operational period is presented in chromatographic form for the flame ionization detectable substances in Figures 134-138 and for the electron capture detectable substances in Figures 140-144. Each series begins with the first week of the operational period with subsequent figures representing the efficiency of GAC filtration at three month intervals of continuous operation. A chromatographic profile of the nondisinfected influent is included in each figure as changes in influent concentrations may affect removal efficiencies. Review of these chromatograms for the flame ionization detectable substances indicates, in general, that despite the varing extent of semivolatiles by-product formation and semivolatile organic removal observed for the various disinfectants under study, virtually identical removals were observed for GAC filtration in each process stream. These removals were essentially constant with no evidence of breakthrough as indicated by the TFIC's in the effluent of each GAC and GAC duplicate column which are presented in Figure 139 covering a period from day 157 to the end of the operational period. The average TFIC removals observed for the GAC and GAC duplicate columns during this period ranged from 47-55% with effluent concentrations ranging from 1.45 - 1.73 ug/l as 1-chlorododecane. Examination of the electron capture GC profiles in Figures 140-144 indicates that although similiar removals were observed for the combined GAC effluents of each process stream during the first three months of operation, breakthrough was observed for the chlorine process stream prior to six months of operation as indicated by the increasing areas at the beginning of chromatograms. Although difficult to visualize in these chromatograms, a low level of breakthrough was also observed around this same time for the chloramine GAC columns as indicated by the TECC's depicted in Figure 145. Unfortunately the exact time of breakthrough could not be determined as the TECC data was not recorded until day 157. The average removals observed for the combined effluents of the GAC and GAC duplicate columns in the nondisinfected, ozone, and chlorine dioxide process streams were essentially identical at

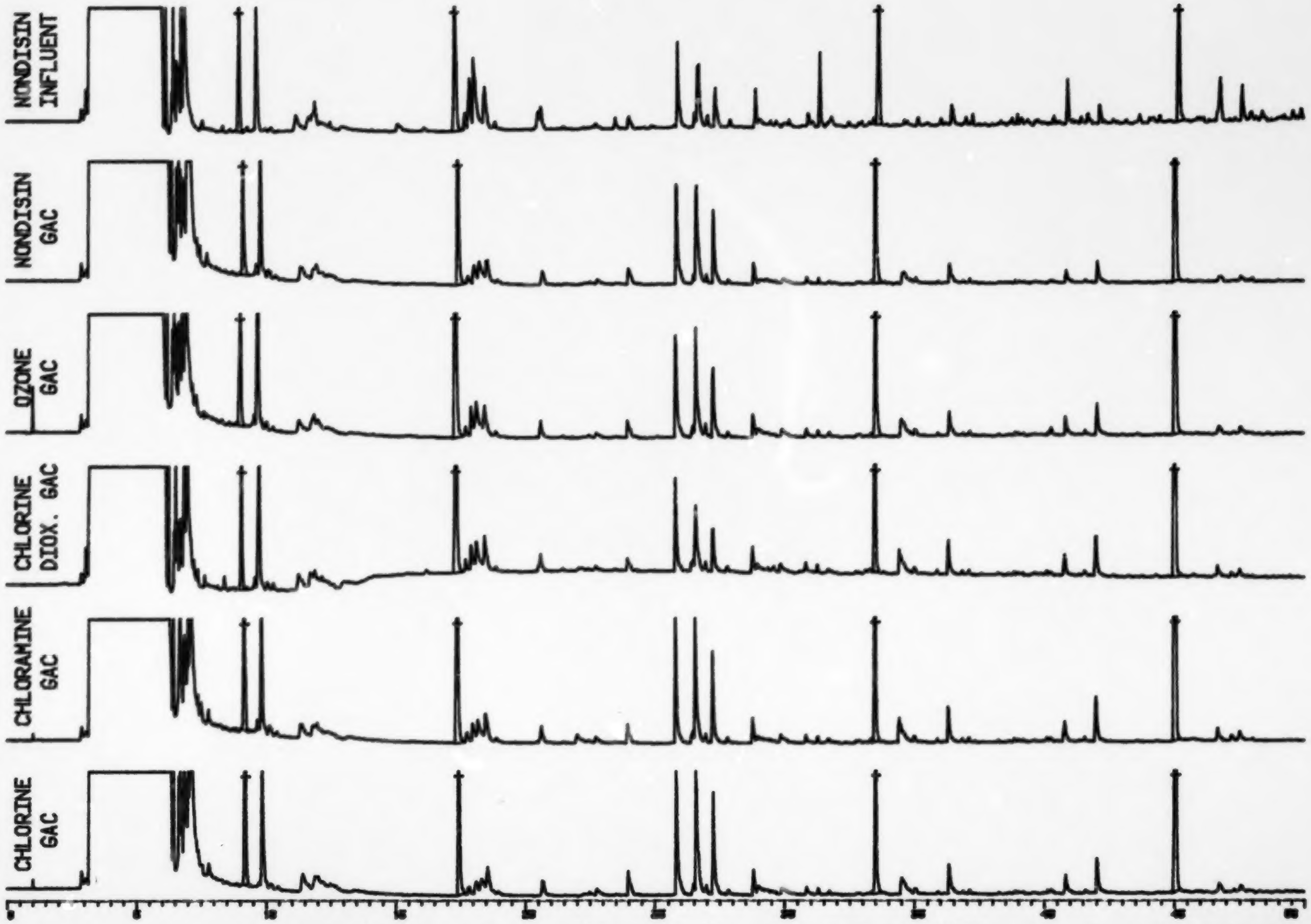


Figure 134. Flame Ionization GC Profiles of the GAC Column Effluent of each Process Stream During the First Week of Operation.

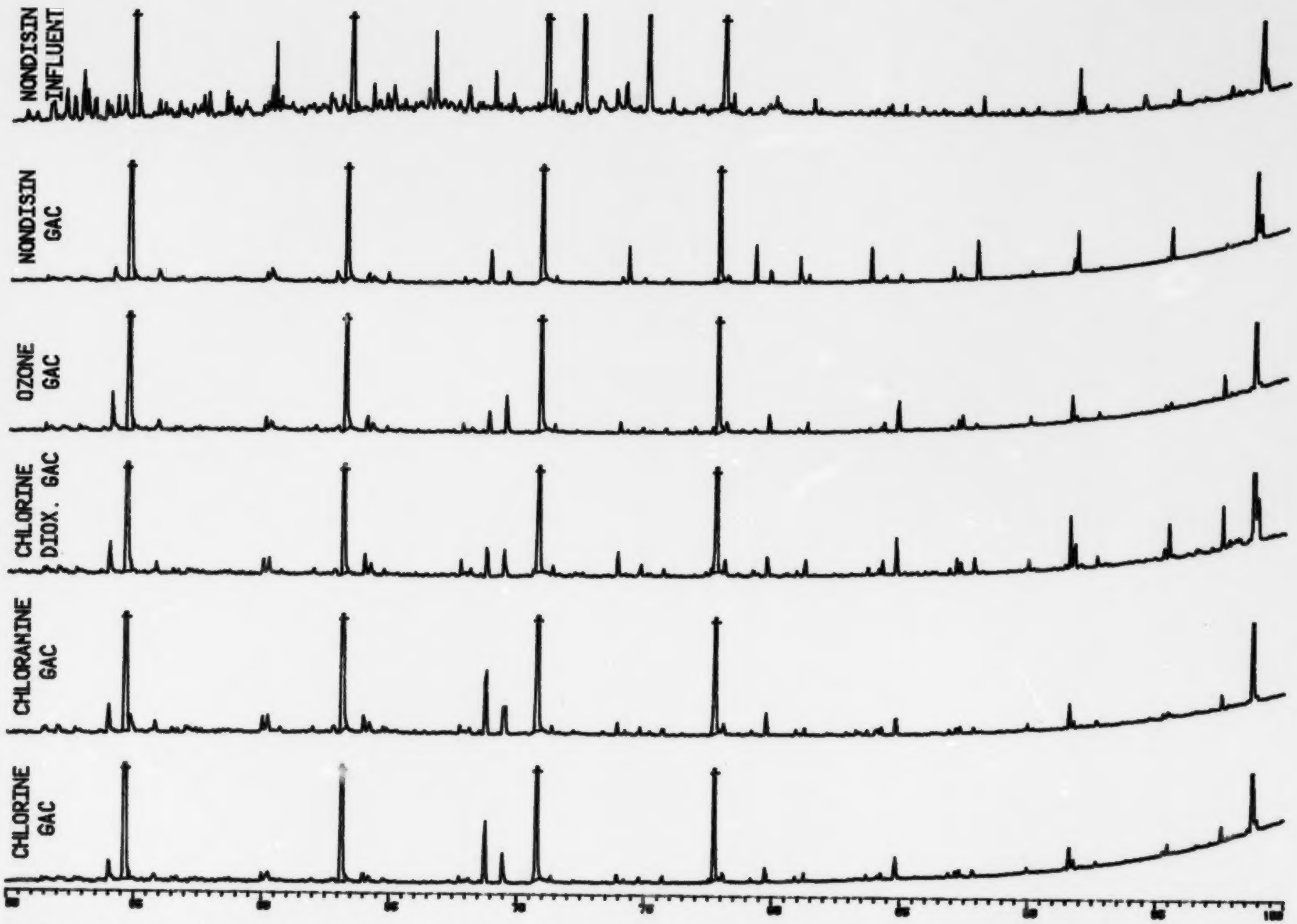


Figure 134. (Cont.) Flame Ionization GC Profiles of the GAC Column Effluent of each Process Stream During the First Week of Operation.

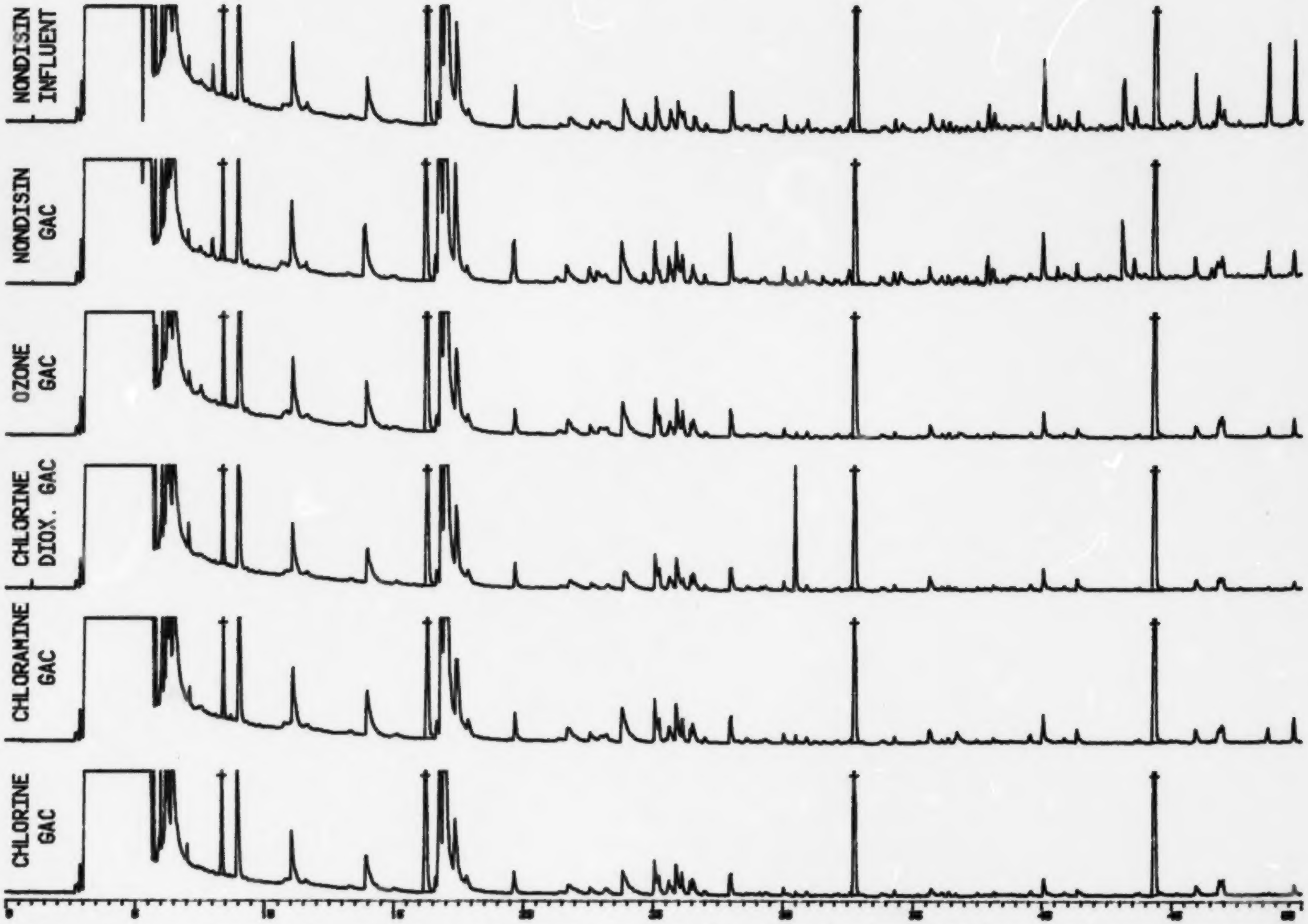


Figure 135. Flame Ionization GC Profiles of the GAC Column Effluent of each Process Stream After 3 Months of Operation.

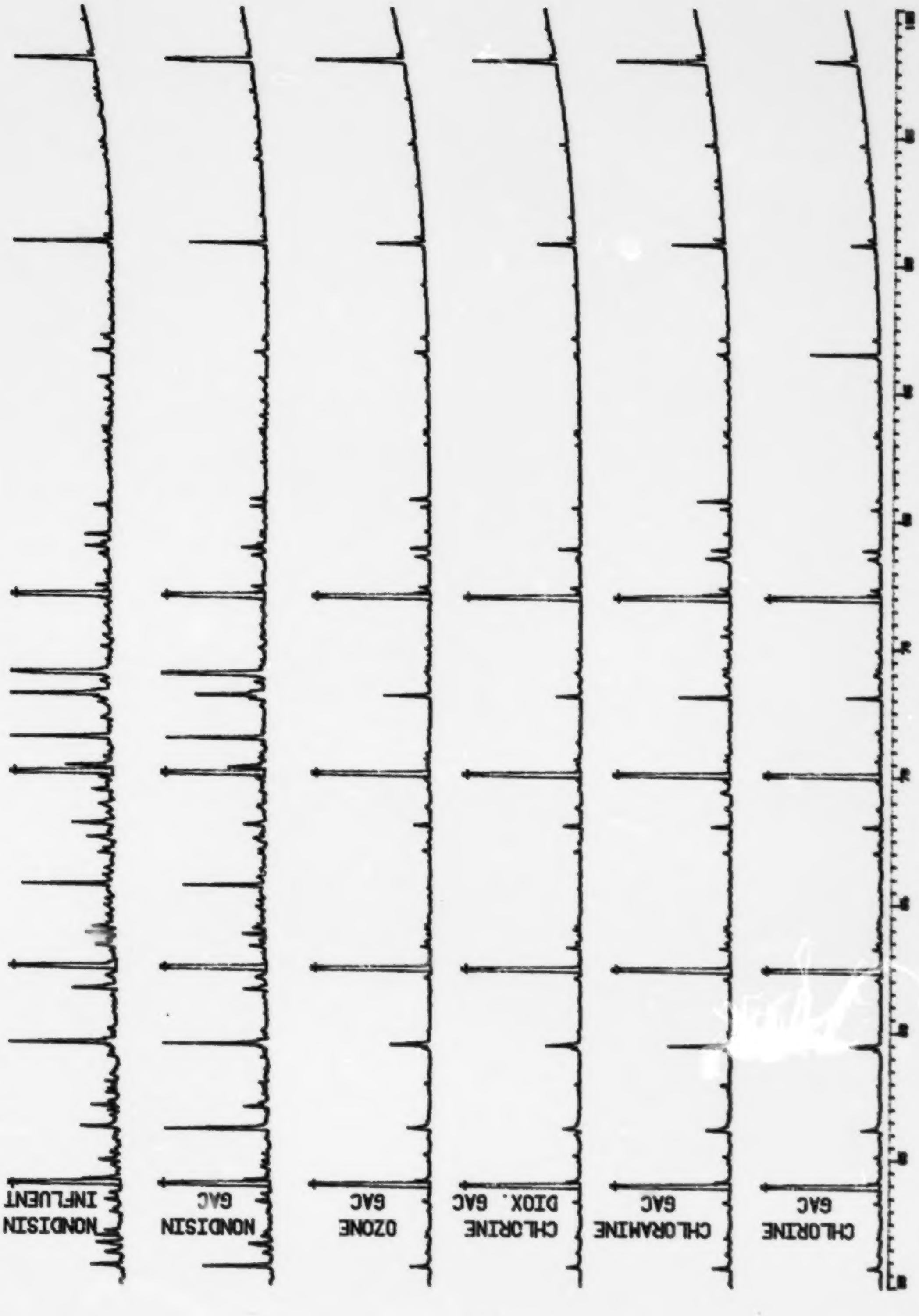


Figure 135. (Cont.) Flame Ionization GC Profiles of the GAC Column Effluent of each Process Stream After 3 Months of Operation.

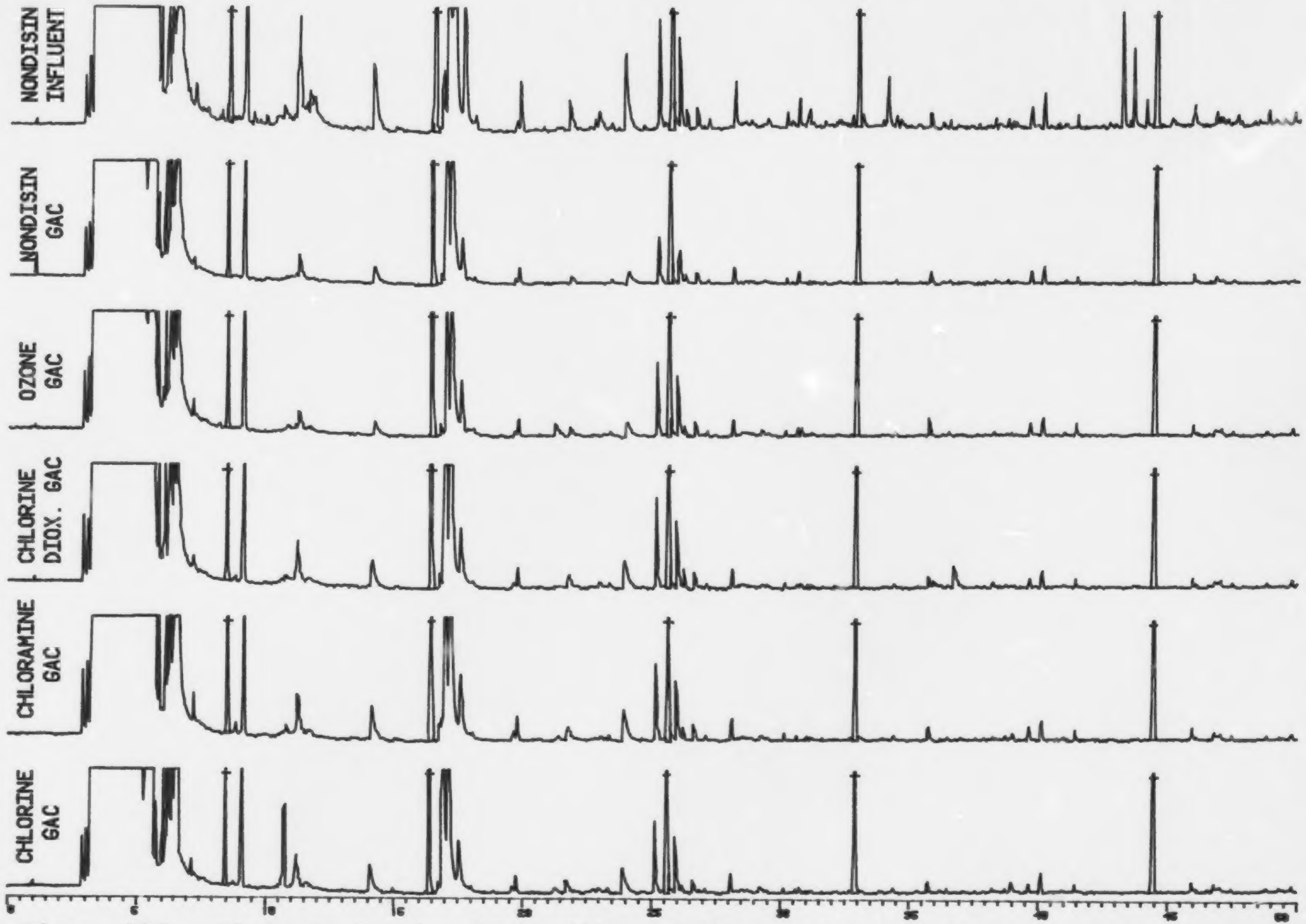


Figure 136. Flame Ionization GC Profiles of the GAC Column Effluent of each Process Stream After 6 Months of Operation.

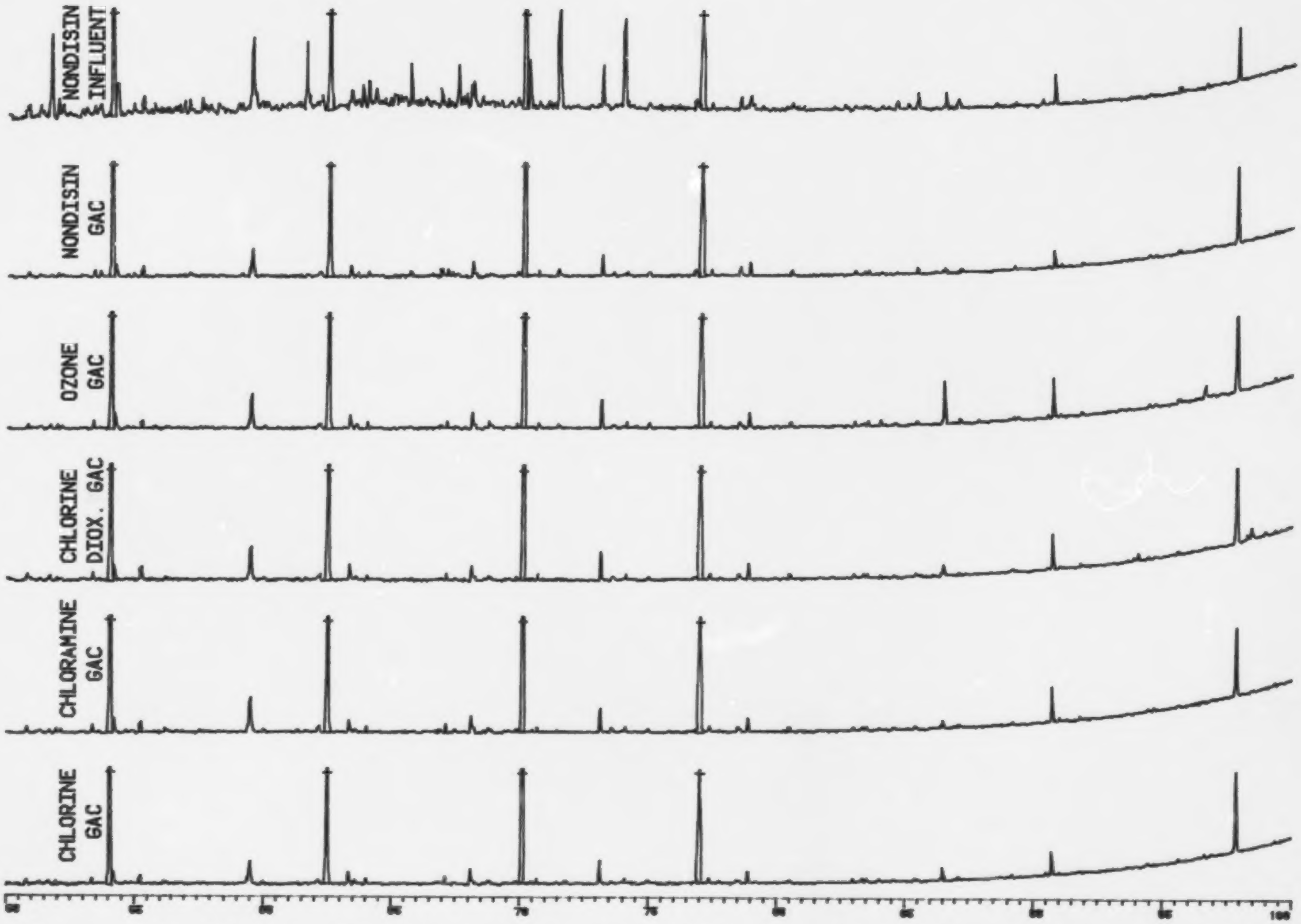


Figure 136. (Cont.) Flame Ionization GC Profiles of the GAC Column Effluent of each Process Stream After 6 Months of Operation.

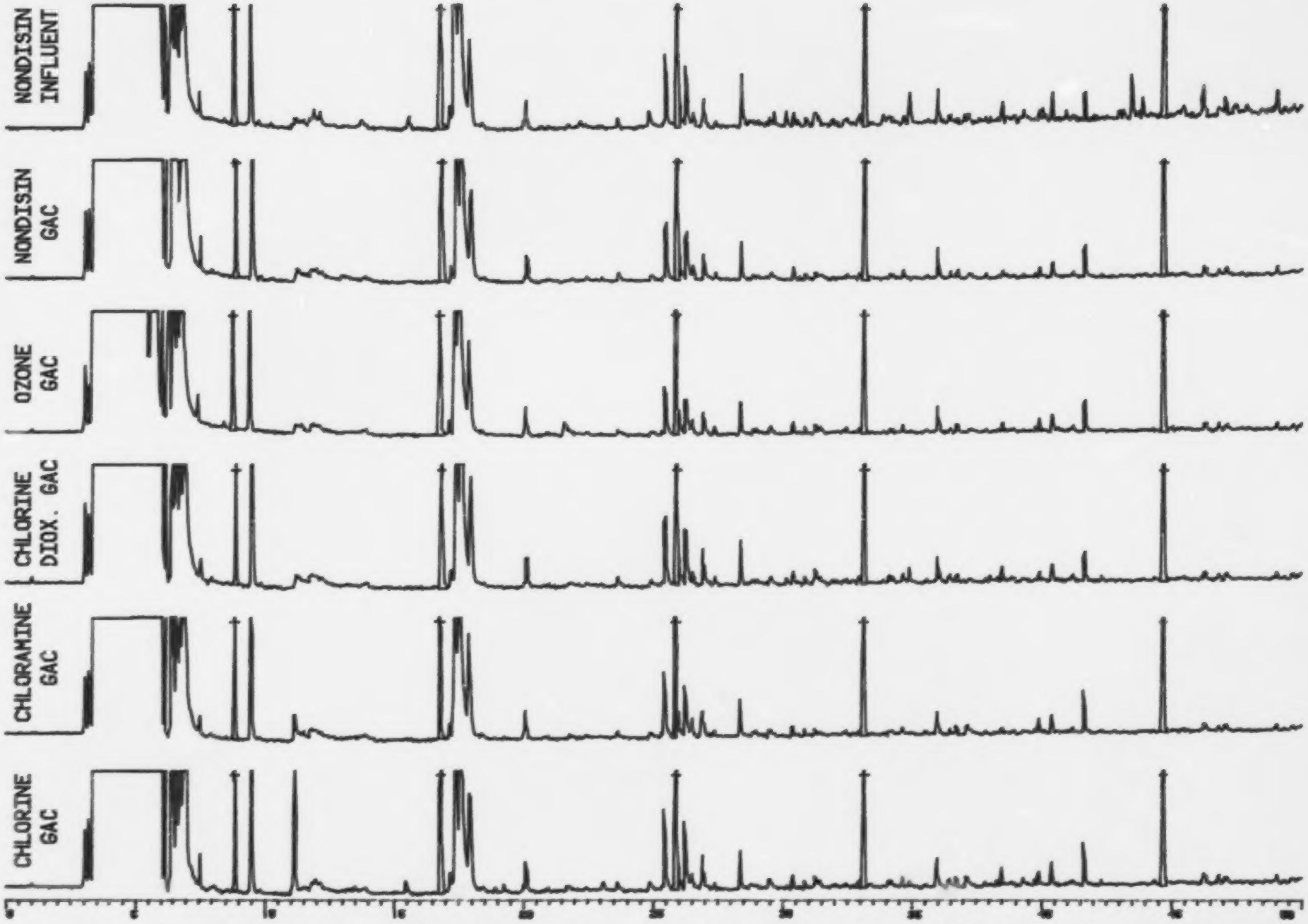


Figure 137. Flame Ionization GC Profiles of the GAC Column Effluent of each Process Stream After 9 Months of Operation.

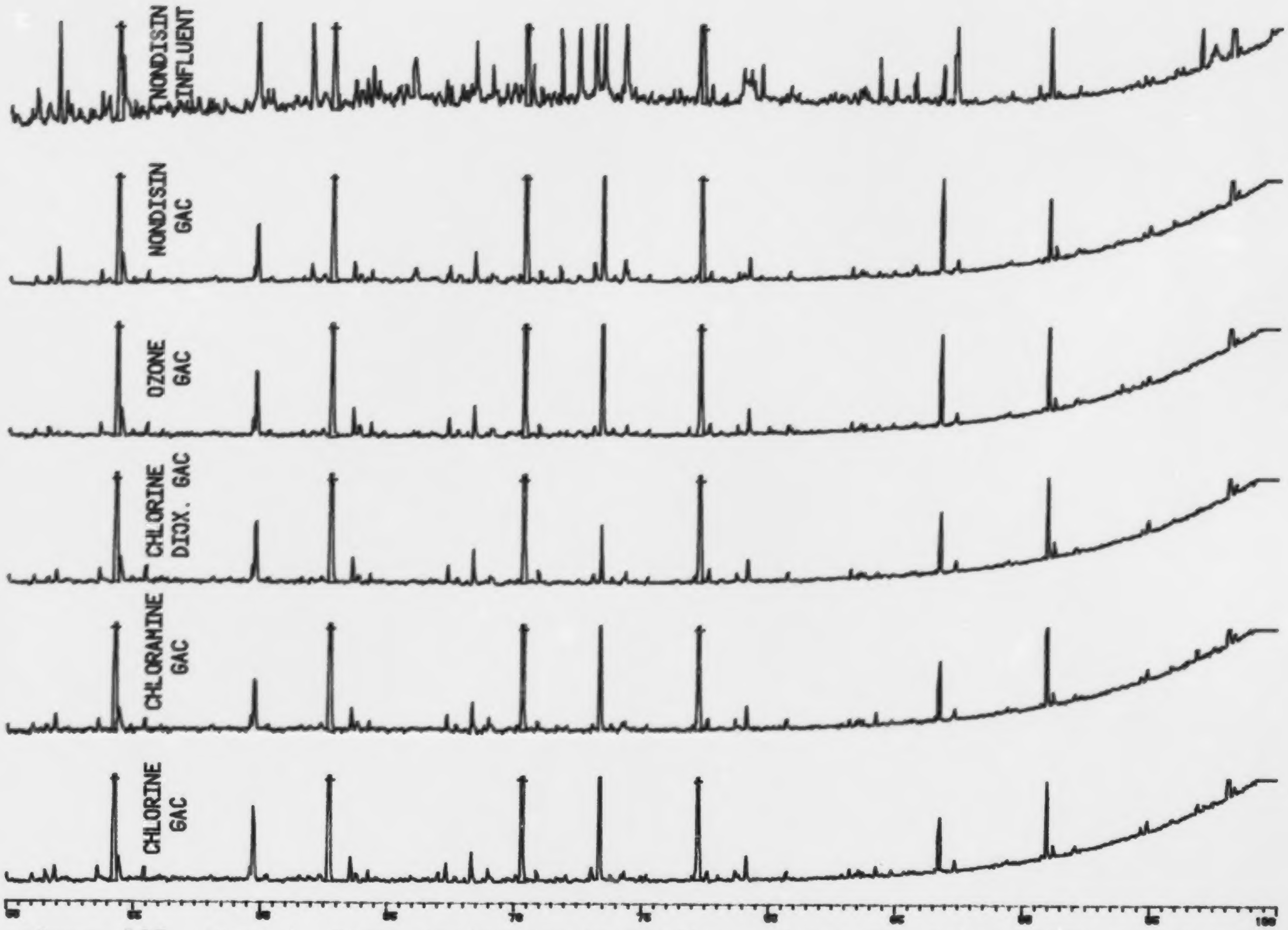


Figure 137. (Cont.) Flame Ionization GC Profiles of the GAC Column Effluent of each Process Stream After 9 Months of Operation.

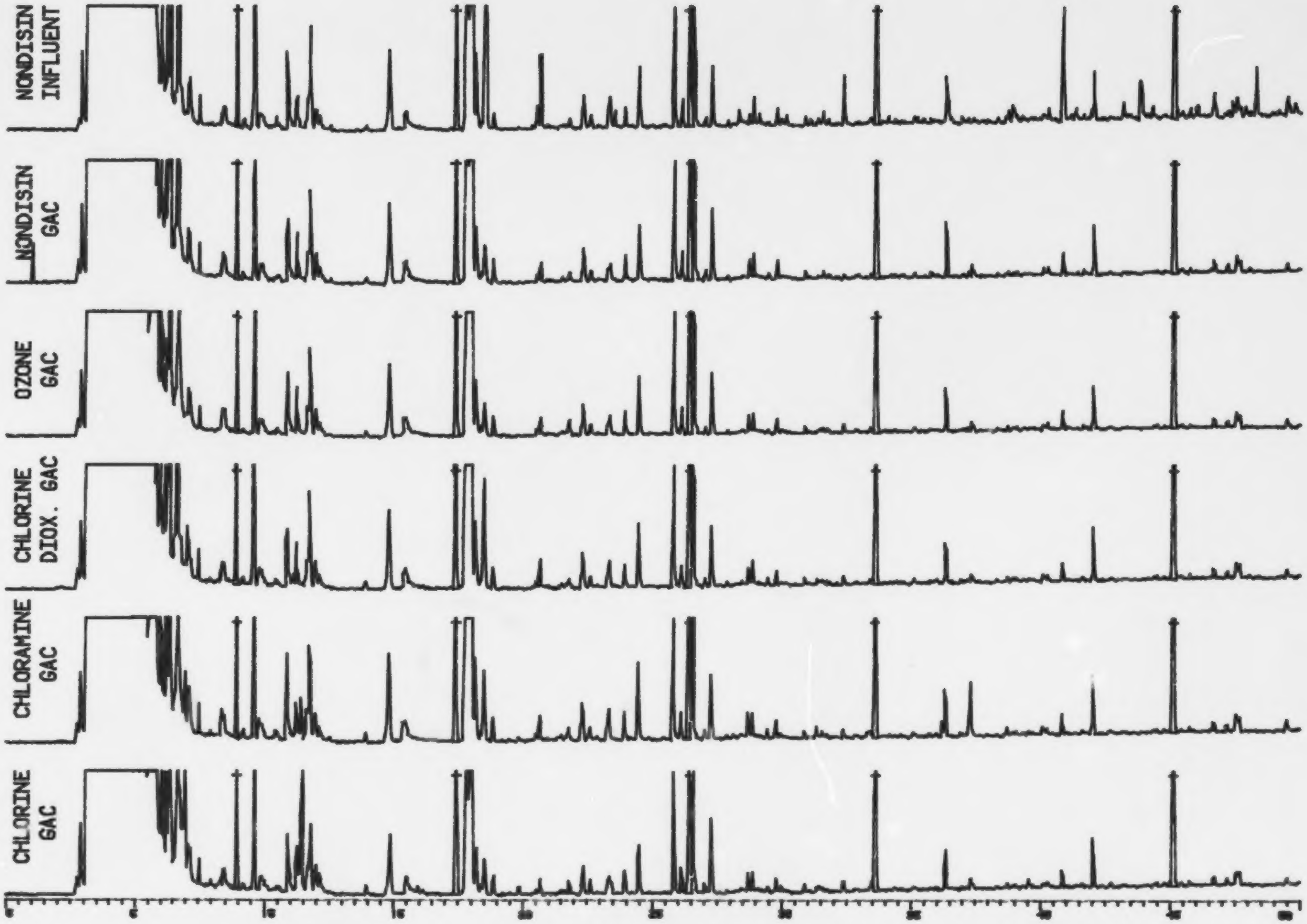


Figure 138. Flame Ionization GC Profiles of the GAC Column Effluent of each Process Stream After 12 Months of Operation.

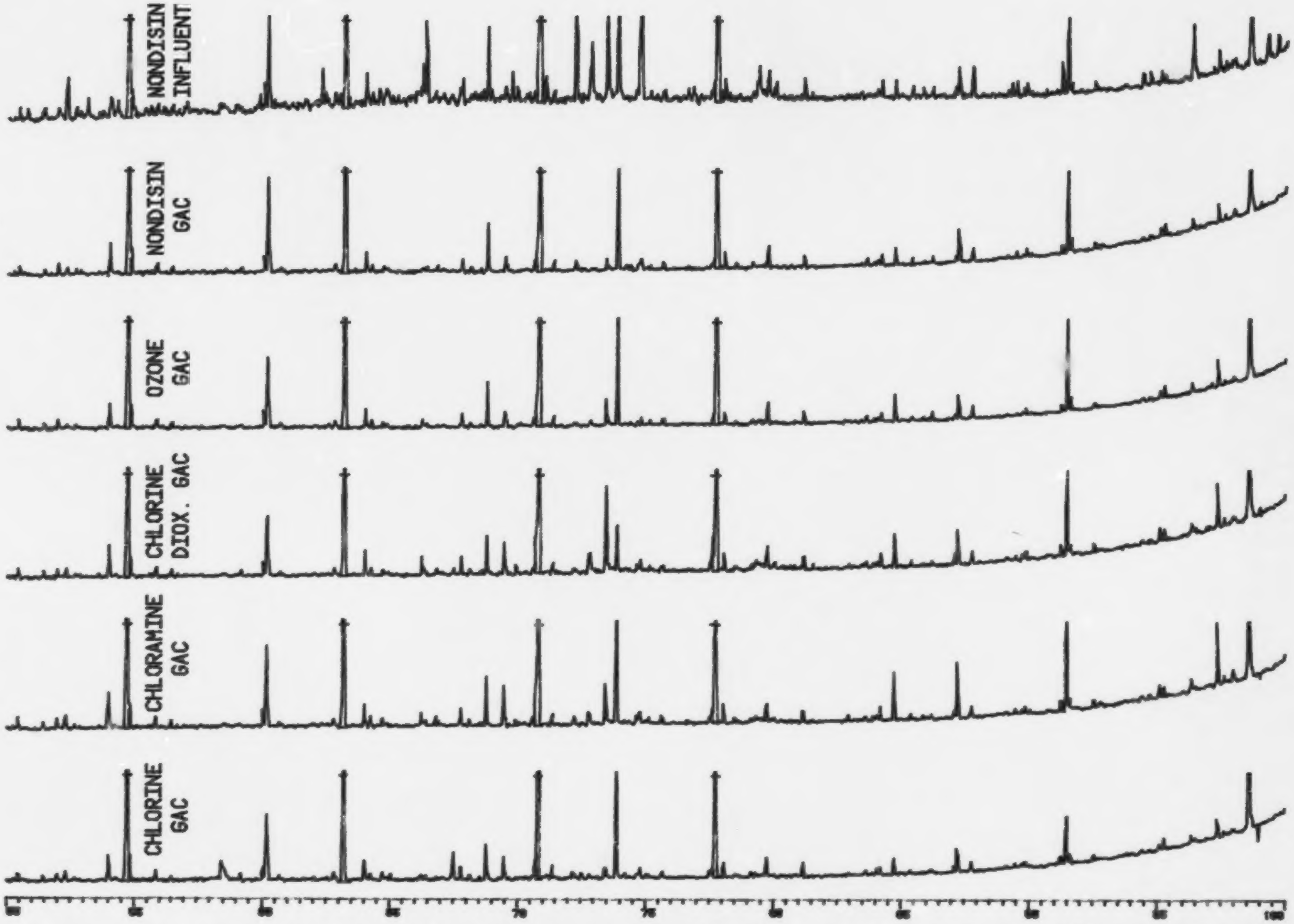


Figure 138. (Cont.) Flame Ionization GC Profiles of the GAC Column Effluent of each Process Stream After 12 Months of Operation.

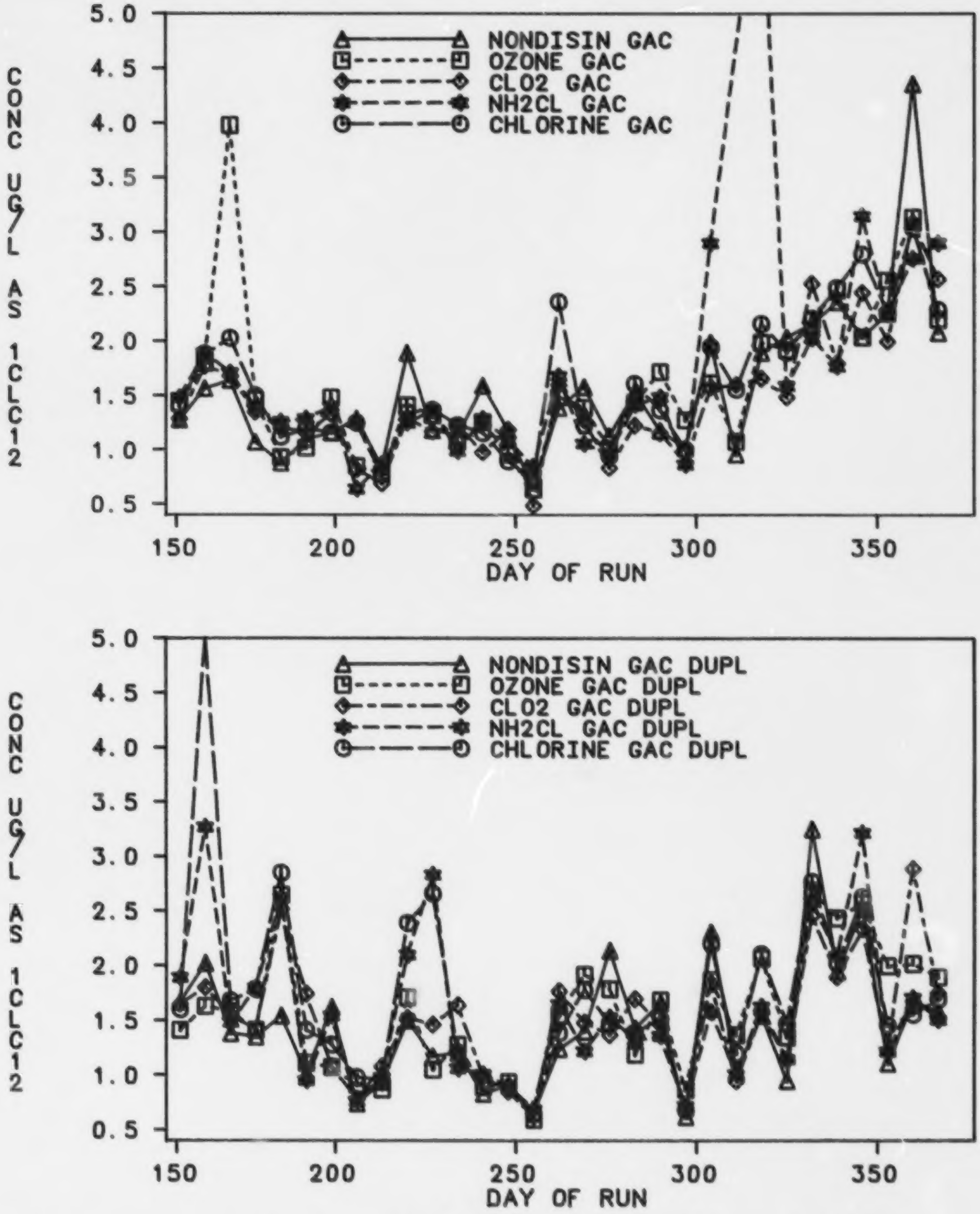


Figure 139. Total Flame Ionization Concentrations in the Effluent of the GAC and GAC Duplicate Columns of each Process Stream.

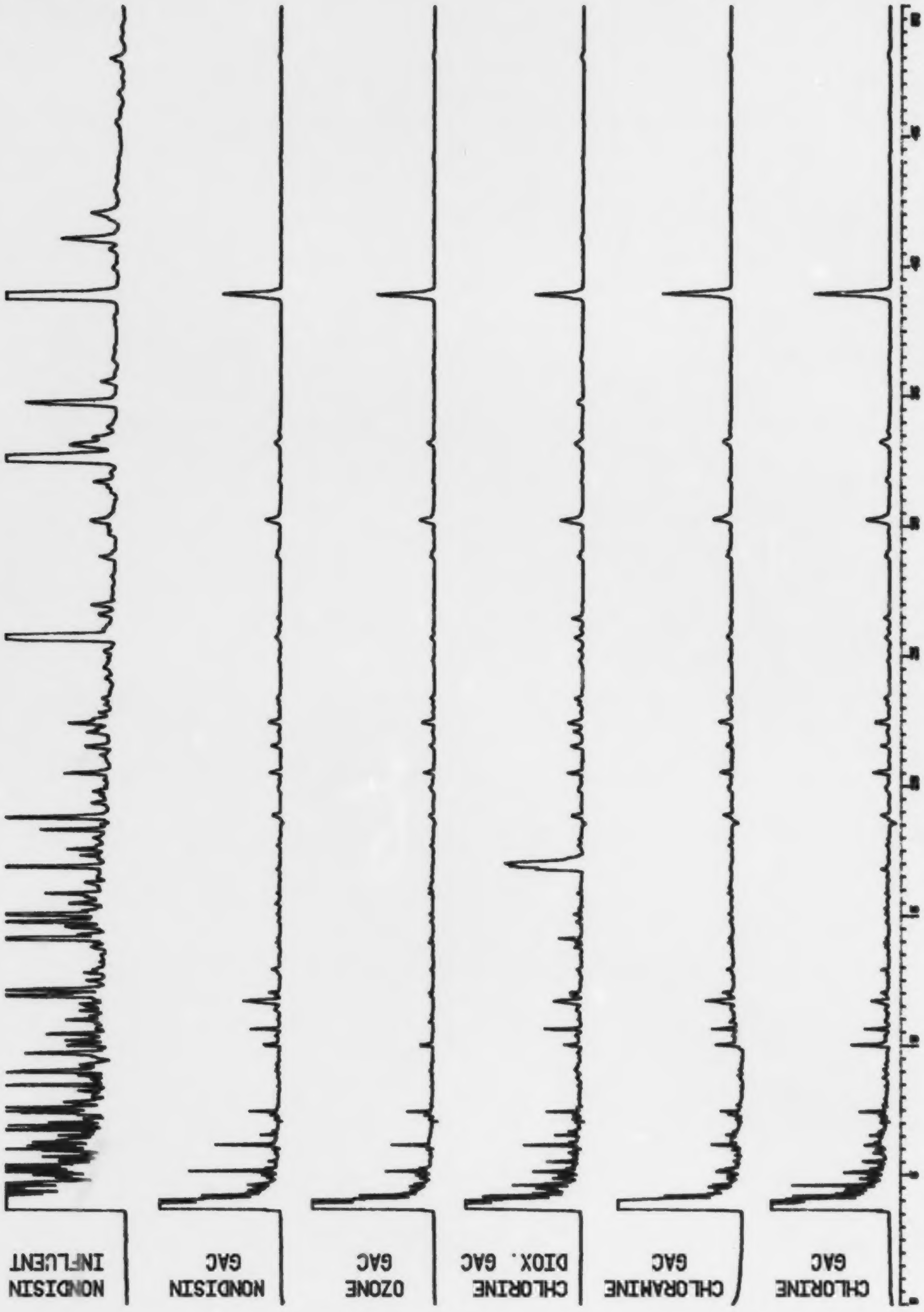


Figure 140. Electron Capture GC Profiles of the GAC Column Effluent of each Process Stream During the First Week of Operation.

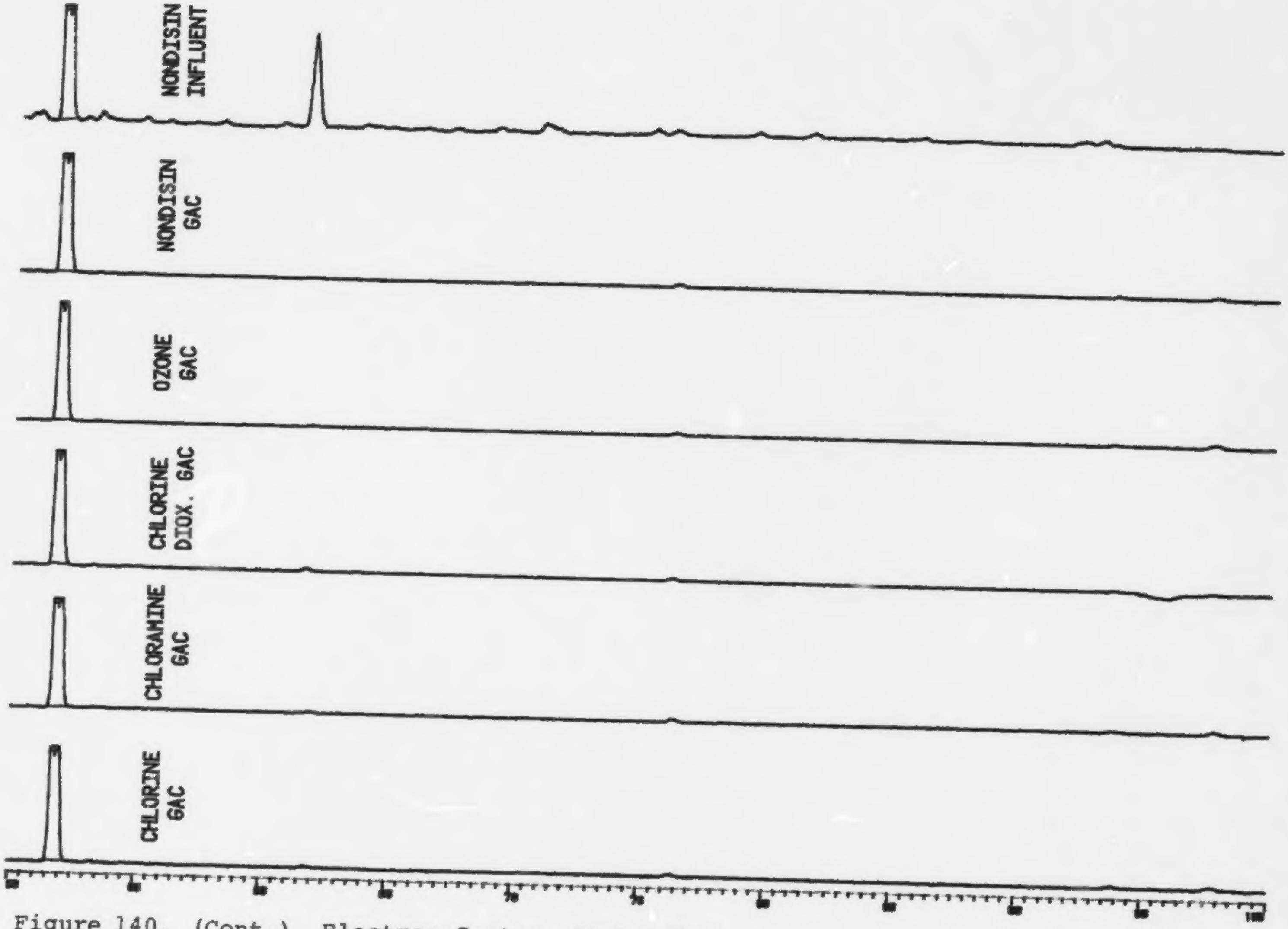


Figure 140. (Cont.) Electron Capture GC Profiles of the GAC Column Effluent of each Process Stream During the First Week of Operation.

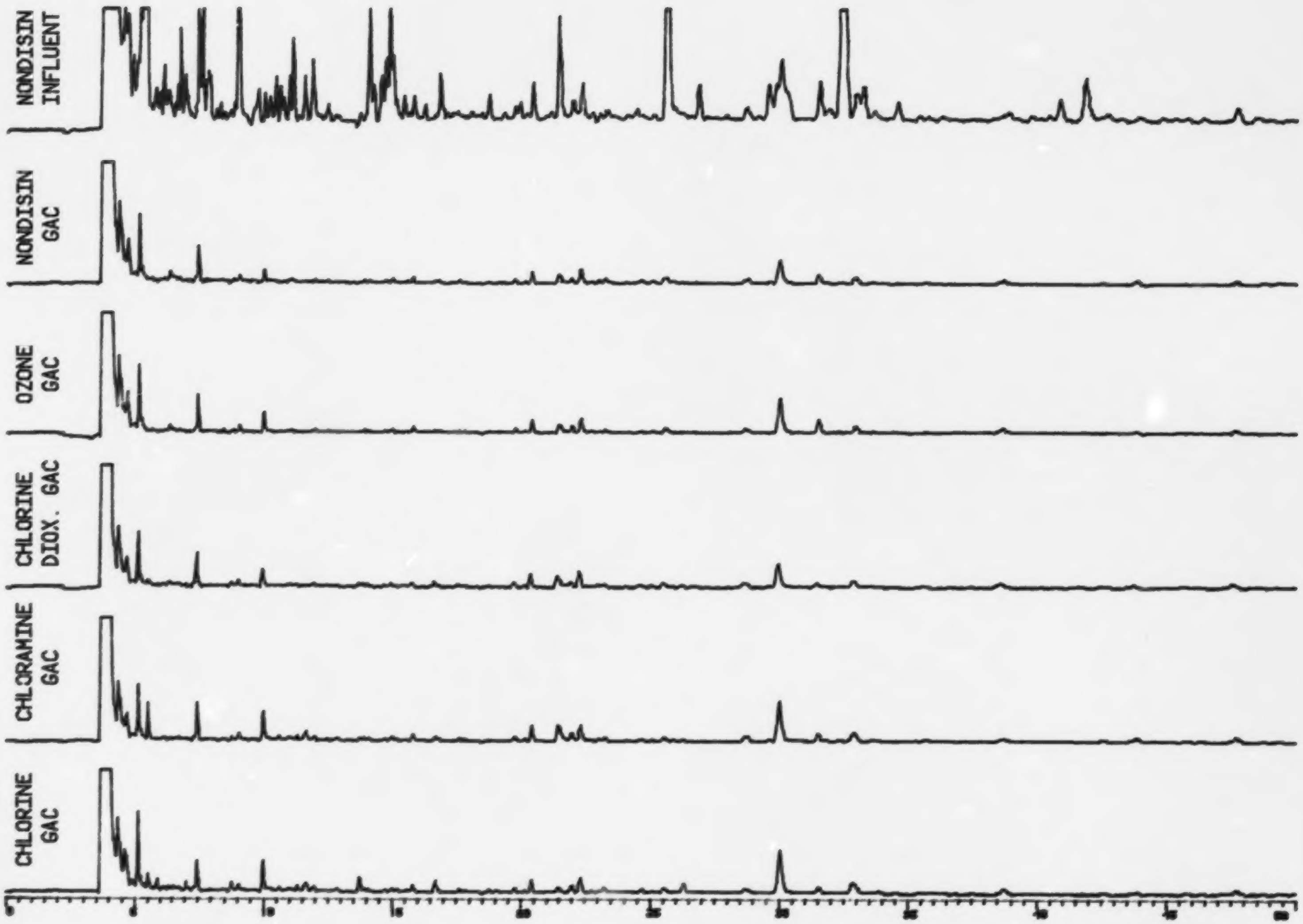


Figure 141. Electron Capture GC Profiles of the GAC Column Effluent of each Process Stream After 3 Months of Operation.

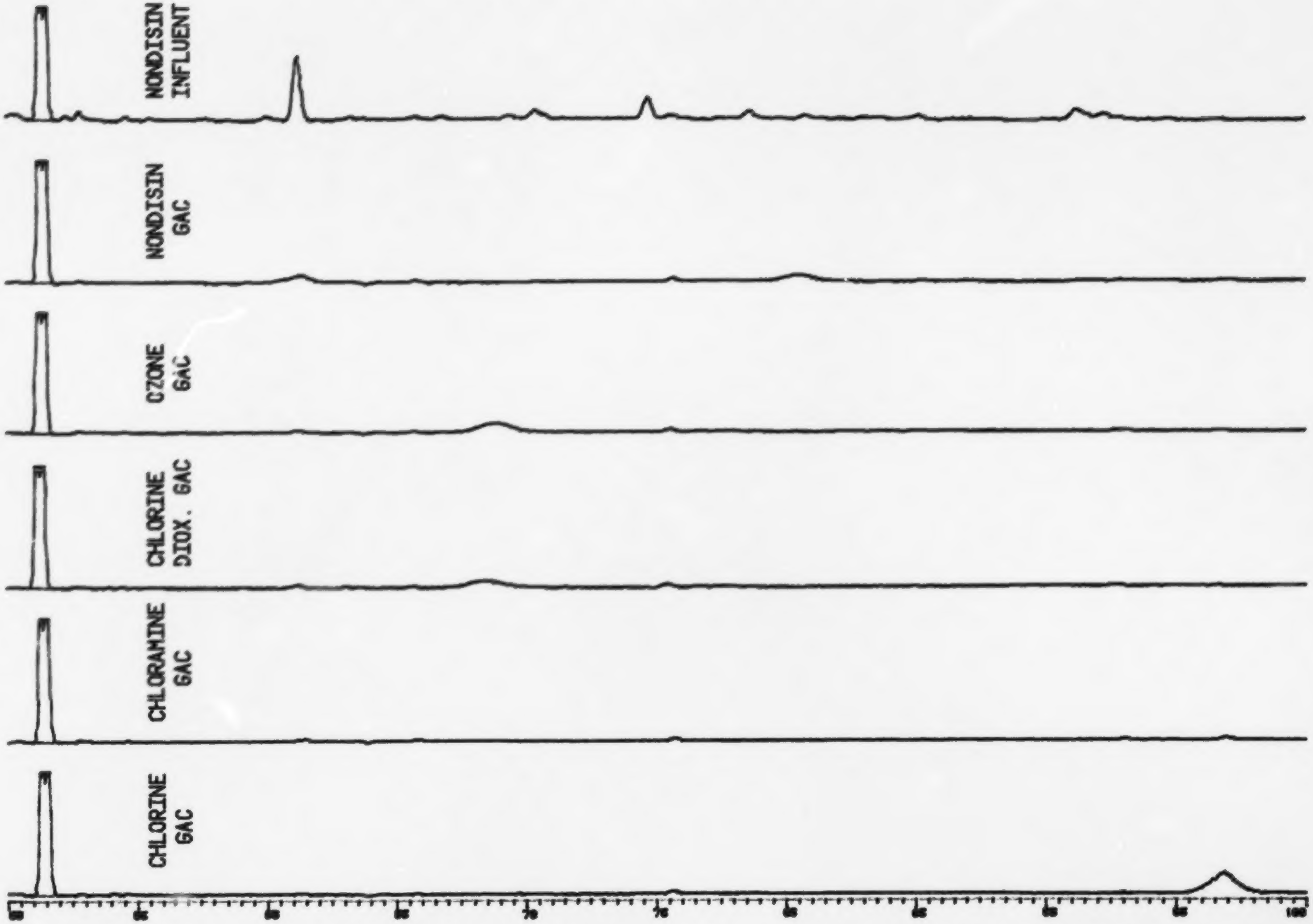


Figure 141. (Cont.) Electron Capture GC Profiles of the GAC Column Effluent of each Process Stream After 3 Months of Operation.

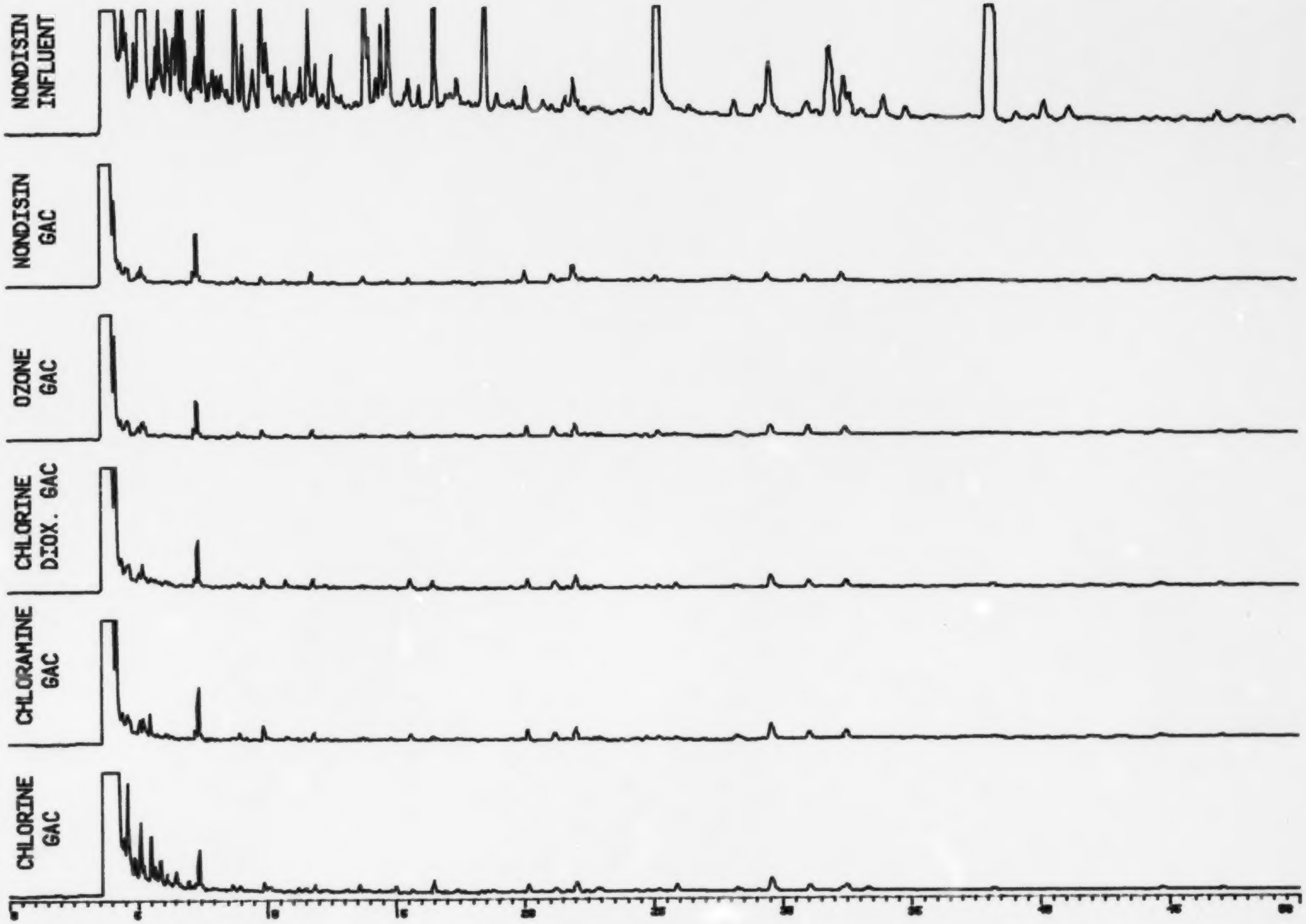


Figure 142. Electron Capture GC Profiles of the GAC Column Effluent of each Process Stream After 6 Months of Operation.

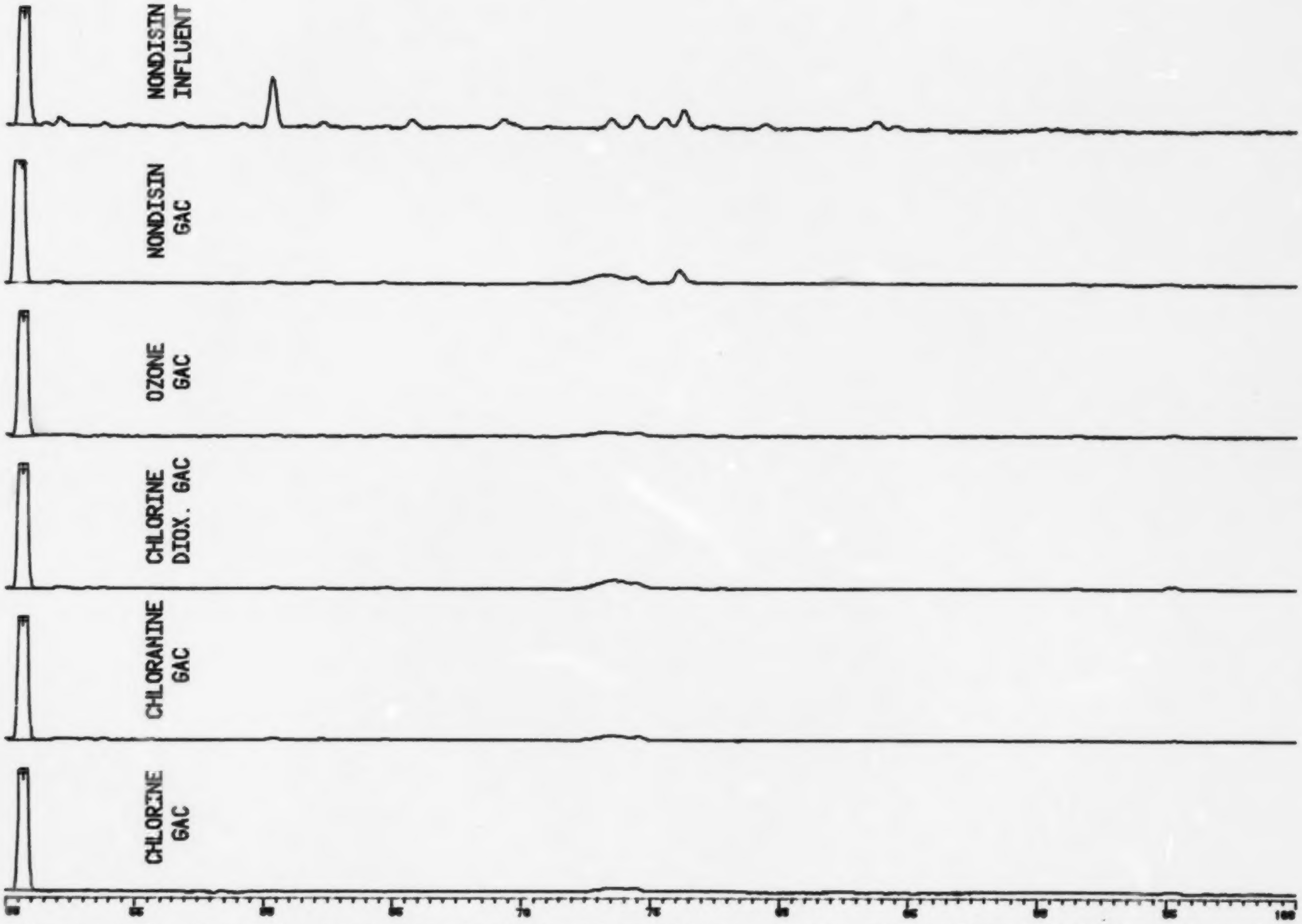


Figure 142. (Cont.) Electron Capture GC Profiles of the GAC Column Effluent of each Process Stream After 6 Months of Operation.

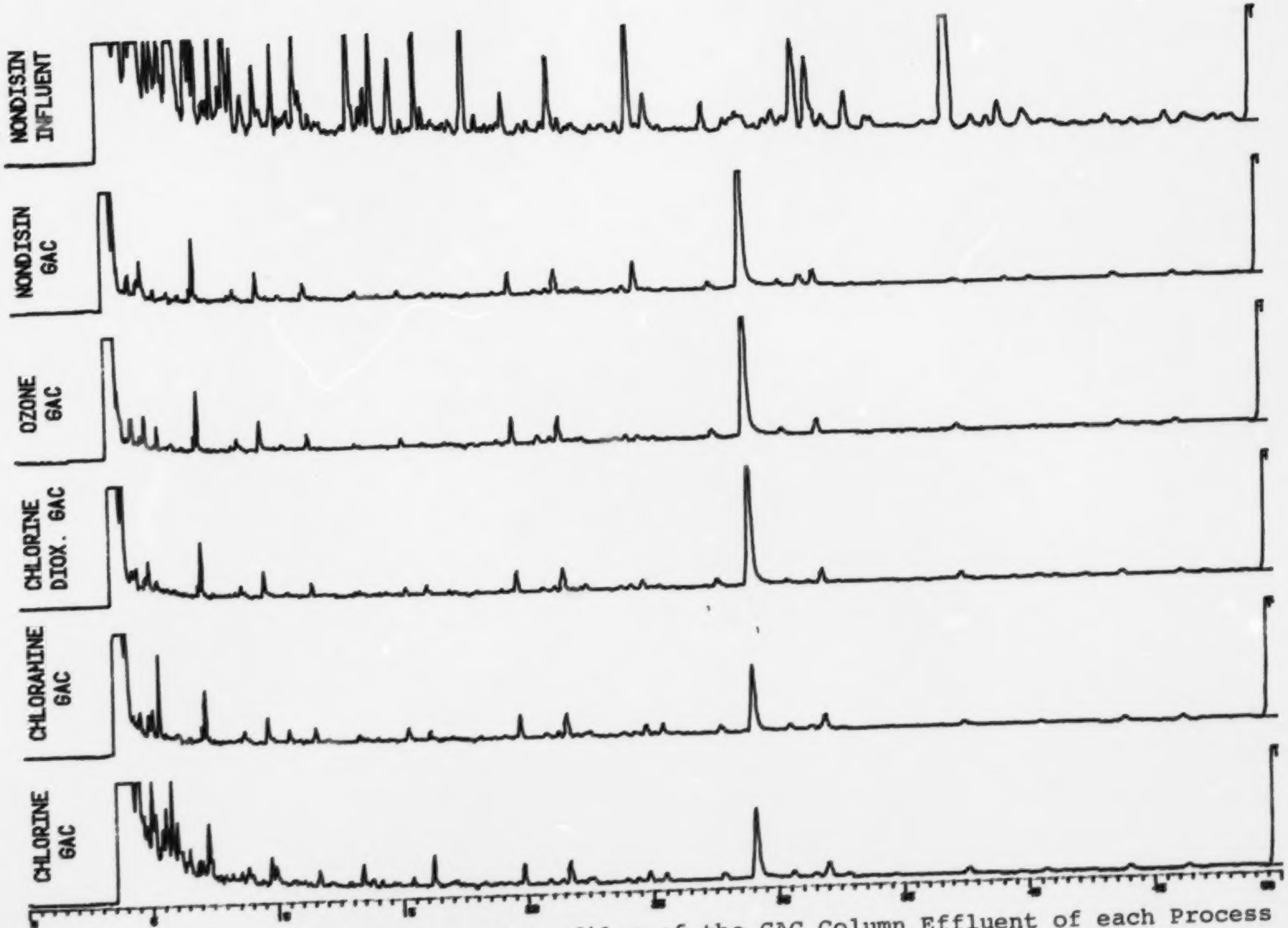


Figure 143. Electron Capture GC Profiles of the GAC Column Effluent of each Process Stream After 9 Months of Operation.

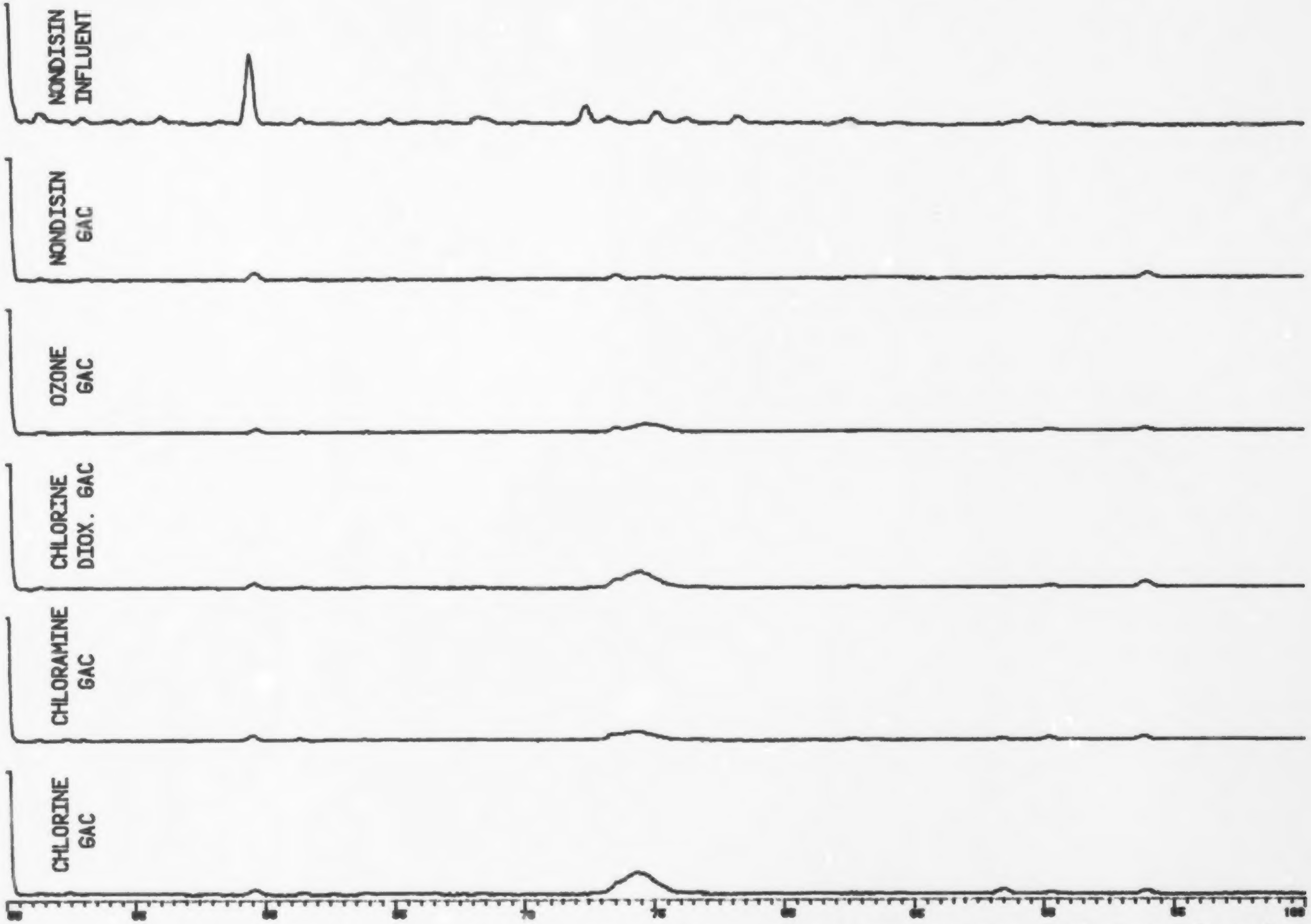


Figure 143. (Cont.) Electron Capture GC Profiles of the GAC Column Effluent of each Process Stream After 9 Months of Operation.

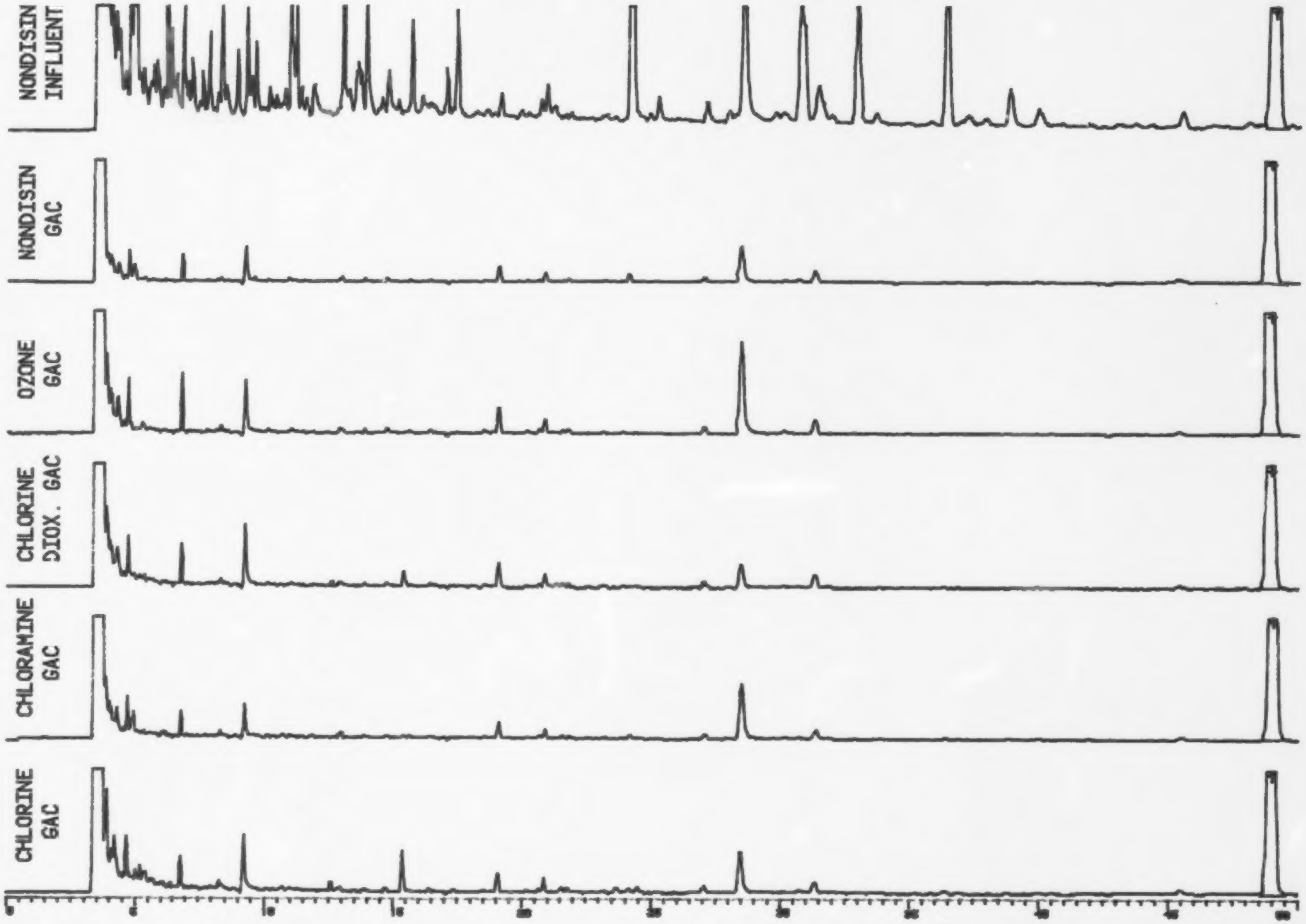


Figure 144. Electron Capture GC Profiles of the GAC Column Effluent of each Process Stream After 12 Months of Operation.

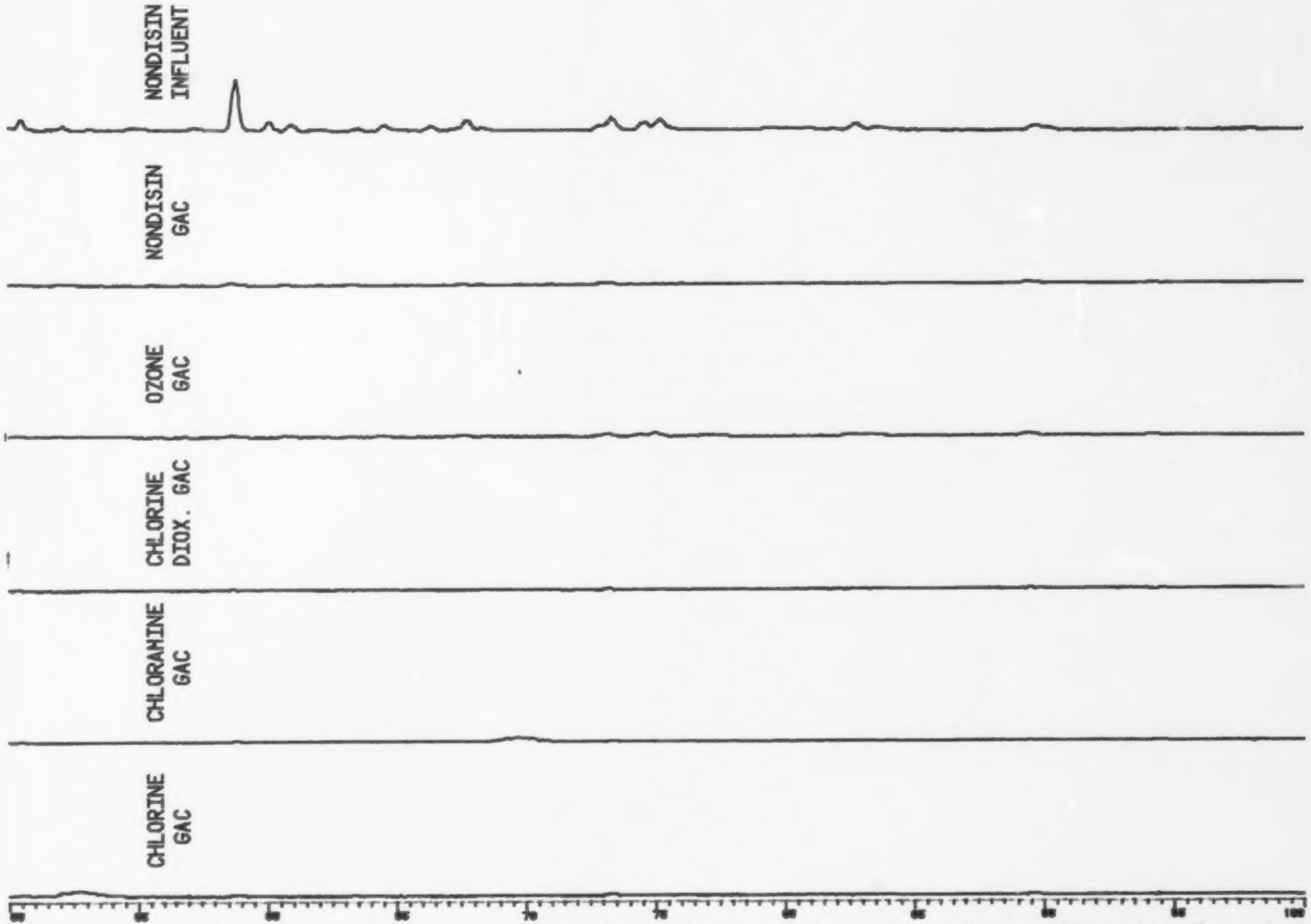


Figure 144. (Cont.) Electron Capture GC Profiles of the GAC Column Effluent of each Process Stream After 12 Months of Operation.

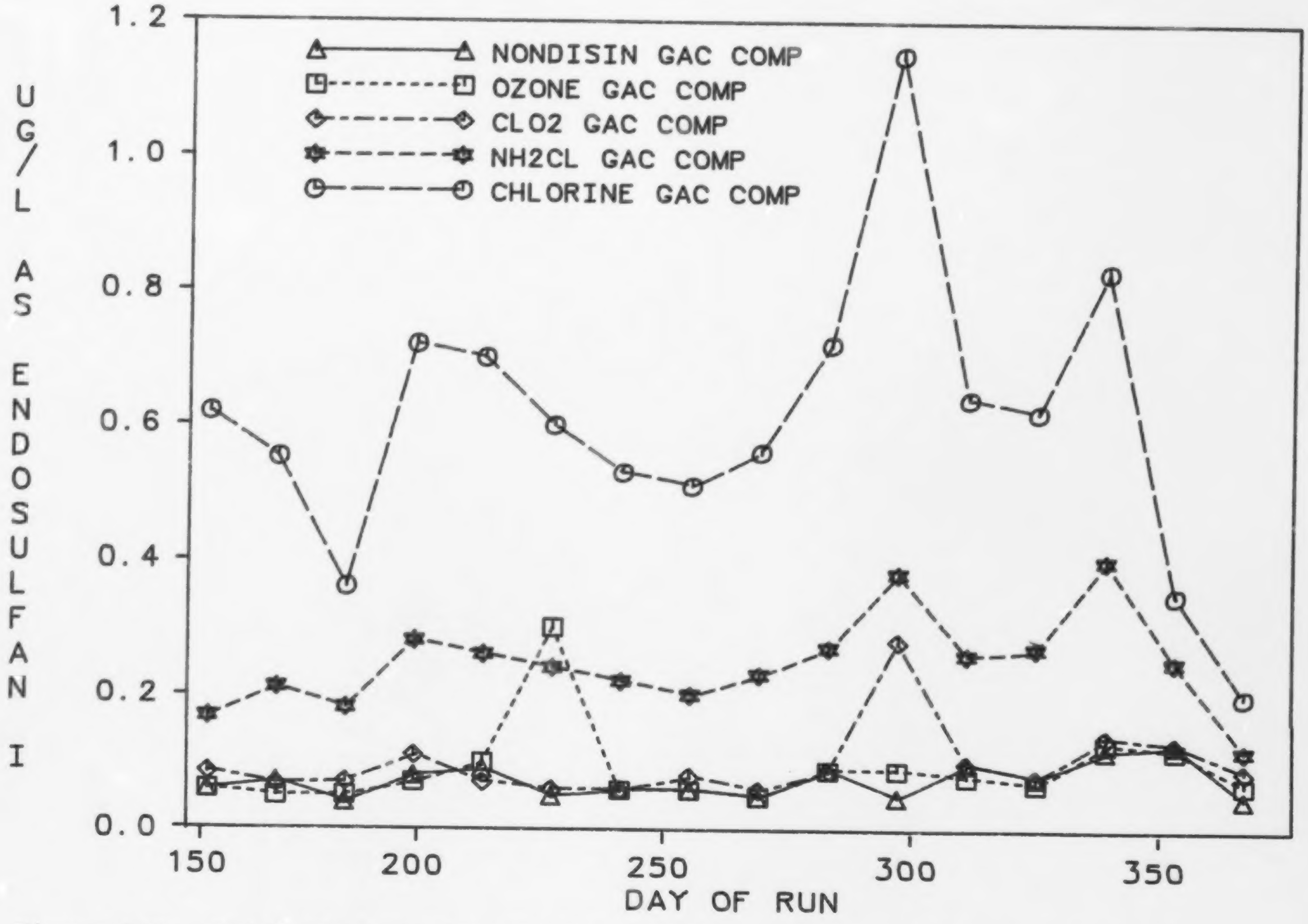


Figure 145. Total Electron Capture Concentrations in the Combined GAC and GAC Duplicate Effluents of each Process Stream.

79, 73, and 72% respectively, with average TECC's of 0.074, 0.090, and 0.098 ug/l as endosulfan I. With an average TECC of 0.245 ug/l as endosulfan I, an average removal of 75% was observed for the combined chloramine GAC and GAC duplicate columns with respect to the chloramine influent, however, the removal with respect to the nondisinfected influent was only 29%. As discussed in earlier sections of this report, it is probable that the GAC effluent TECC's of the chloramine system would have been very similiar to those of the chlorine dioxide system had chloramines been generated in the absence of free chlorine. The average effluent TECC of the combined chlorine GAC and GAC duplicate columns was 0.504 ug/l as endosulfan I which corresponds to an average removal of 74% with respect to the chlorine influent, however, this represents an average increase of 43% with respect to the nondisinfected influent.

A number of disinfection by-products have been tentatively identified using a Finnigan 4000 GC/MS/DS in conjunction with the 32,000 compound NBS Library supplied with this instrument. Those ozonation by-products observed were straight chain as well as branched chain alkylaldehydes from hexanal to pentadecanal and 6,10,14-trimethyl-2-pentadecanone. There were no chlorine dioxide by-products identified, however, all of the chromatographic peaks produced were common to those produced by chlorination. The only by-product tentatively identified in the chloramine influent was the pentylester of nitric acid. This substance as well as the other chromatographic peaks produced by chloramination were also common to those produced by chlorination. Those chlorinated by-products generated in the chlorination process were 1-chloro-2-methyl-2-butene; 2,3-dichloro-2-methylbutane; 1,1,1-trichloro-2-propanone; 2-bromohexane; and hexachlorocyclopentadiene while those nonchlorinated by-products generated were 2-methypropanol; 1-ethylpropyl hydroperoxide; the pentylester of nitric acid; and 3 isomers of 2,2'-[ethylindene-bis(oxy)] bis-pentane. It should be noted that none of the aforementioned by-products have been confirmed by authentic external standards.

SUMMARY OF THE EFFECTS OF PREDISINFECTION AND GAC FILTRATION ON AVERAGE WATER QUALITY

The over all effects of alternative disinfection preceeding sand filtration and GAC filtration are summarized in Tables 31-33 with each table representing a subsequent step in the process stream. In these tables, the average concentration of each parameter in the nondisinfected influent is compared with those observed in the effluent of each process step. The average percent change in concentration is also indicated relative to the nondisinfected influent. However, the average percent change in many instances did not correlate well with average concentration

TABLE 31. SUMMARY OF THE EFFECTS OF 30 MINUTES OF DISINFECTANT CONTACT TIME WITH THE ALTERNATE DISINFECTANTS OVER THE ONE YEAR OPERATIONAL PERIOD

PARAMETER	AVERAGE NONDISIN. INFLUENT CONC. (UG/L)	FINAL AVERAGE CONC. IN UG/L (AVE. PERCENT CHANGE)			
		OZONE INFLUENT	CHLORINE DIOXIDE INFLUENT	CHLORAMINE[1] INFLUENT	CHLORINE INFLUENT
TOC	3330	3040(-9%)	3276(NC[2])	3353(NC)	3267(NC)
TOX	25	15(-40%)	85(+240%)	117(+347%)	263(+952%)
TFIC [3,4]	3.9	2.0(-41%)	3.8(NC)	4.47(+17%)	18.3(+245%)
THM	1.3	1.1(NC)	1.3(NC)	4.5(+809%)	34(+2515%)
1,2-dichloro-ethane	0.6	0.6(NC)	0.6(NC)	0.7(NC)	0.7(NC)
Total alkylbenzene	0.586	0.099(-52%)	0.609(+11%)	0.607(+14%)	0.783(+100%)
TECC [3,5]	0.380	0.23(-40%)	0.44(+11%)	1.05(+165%)	2.35(+495%)
Total phthalate	0.179	0.158(-11%)	0.143(NC)	0.181(NC)	0.142(NC)
Total PNAH	0.144	0.033(-74%)	0.139(NC)	0.145(NC)	0.118(NC)
alachlor	0.127	0.009(-84%)	0.119(NC)	0.120(NC)	0.116(NC)
Total chlorobenzene	0.103	0.039(-58%)	0.102(NC)	0.105(NC)	0.205(+75%)
atrazine	0.064	0.009(-83%)	0.076(NC)	0.081(NC)	0.094(NC)
4-nonylphenol	0.059	0.009(-72%)	0.031(-46%)	0.045(-19%)	0.025(-54%)
Total alkane	0.045	0.024(-35%)	0.038(NC)	0.043(NC)	0.040(NC)
tributylphosphate	0.041	0.005(-89%)	0.041(NC)	0.042(NC)	0.042(NC)
Total CHI	0.035	0.014(-57%)	0.031(NC)	0.035(NC)	0.031(NC)
Total nitrobenzene	0.027	0.008(-61%)	0.028(NC)	0.021(NC)	0.034(+43%)[6]
Total alkylaldehyde	0.017	0.037(+144%)	0.018(NC)	0.016(NC)	0.059(+55%)
d-fenchone	0.006	0.002(-59%)	0.004(NC)	0.005(NC)	0.012(+133%)
triphenylmethane	0.003	0.002(-38%)	0.003(NC)	0.002(NC)	0.002(-25%)

---

[1] The majority of those by-products formed are attributable to a brief contact with free chlorine.
[2] No significant change relative to the nondisinfected influent.
[3] Averages for the last 210 days of the operational period.
[4] Quantified as 1-chlorododecane.
[5] Quantified as endosulfan-I
[6] Average for days 100-374. No significant increase prior to day 100.

TABLE 32. SUMMARY OF THE COMBINED EFFECTS OF 30 MINUTES OF DISINFECTANT CONTACT TIME WITH THE ALTERNATE DISINFECTANTS AND SAND FILTRATION OVER THE ONE YEAR OPERATIONAL PERIOD.

	FINAL AVERAGE CONCENTRATION IN UG/L (AVE. PERCENT CHANGE)				
PARAMETER	NONDISIN. SAND EFFL.	OZONE SAND EFFL.	CHLORINE DIOXIDE SAND EFFL.	CHLORAMINE[1] SAND EFFL.	CHLORINE SAND EFFL.
TOC	3270(-1.5%)	2526(-24%)	3297(NC)	3329(NC)[2]	3299(NC)
TOX	23(NC)	14(NI)[3]	83(NI)	118(NI)	258(NI)
TFIC[4,5]	2.4(-32%)	1.9(-47%)	3.3(-10%)	4.7(+25%)	8.6(+98%)
THM	1.5(NC)	1.0(NC)	1.5(NC)	6.5(NI)	50(+5893%)
1,2-dichloroethane	0.7(NC)	0.6(NC)	0.7(NC)	0.7(NC)	0.7(NC)
Total alkylbenzene	0.102(-49%)	0.097(NI)	0.241(NI)	0.295(NI)	0.680[7](+20%)
TECC[4,6]	0.322(-12%)	0.197(-48%)	0.388(NC)	0.893(+125%)	2.21(+455%)
Total phthalate	0.123(-20%)	0.165(-9%)	0.131(-16%)	0.140(-12%)	0.123(-21%)
Total PNAH	0.055(-49%)	0.029(NI)	0.144(NC)	0.138(NC)	0.115(NC)
alachlor	0.125(NC)	0.011(NI)	0.121(NC)	0.117(NC)	0.115(NC)
Total chlorobenzene	0.104(NC)	0.037(NI)	0.108(NC)	0.104(NC)	0.151(+43%)
atrazine	0.073(NC)	0.012(NI)	0.076(NC)	0.066(NC)	0.088(NC)
4-nonylphenol	0.043(-33%)	0.010(NI)	0.043(NI)	0.039(42%)	0.025(NI)
Total alkane	0.035(NC)	0.022(NI)	0.041(NC)	0.052(NC)	0.036(NC)
tributylphosphate	0.041(NC)	0.007(NI)	0.044(NC)	0.043(NC)	0.043(NC)
Total CHI	0.036(NC)	0.015(NI)	0.032(NC)	0.036(NC)	0.034(NC)
Total nitrobenzene	0.023(NC)	0.006(NI)	0.028(NC)	0.017(NC)	0.030(NI)[8]
Total alkylaldehyde	0.014(NC)	0.016(NC)	0.020(NC)	0.021(NC)	0.019(NC)
d-fenchone	0.004(NC)	0.002(NI)	0.005(NC)	0.005(NC)	0.007(NC)
triphenylmethane	0.002(NC)	0.001(-53%)	0.003(NC)	0.003(NC)	0.002(NI)

---

[1] The majority of those by-products formed are attributable to a brief contact with free chlorine.

[2] No significant change relative to the nondisinfectant influent.

[3] No significant change relative to the respective column influent.

[4] Averages for the last 210 days of the operational period.

[5] Quantitated as 1-chlorododecane.

[6] Quantitated as 1-endosulfan I.

[7] Estimated due to the erratic nature of the data and varing sample frequency.

[8] Average for days 100-374. No significant increase prior to day 100.

TABLE 33. SUMMARY OF THE COMBINED EFFECTS OF 30 MINUTES OF DISINFECTANT CONTACT TIME WITH THE ALTERNATE DISINFECTANTS AND GAC FILTRATION OVER THE ONE YEAR OPERATIONAL PERIOD.

PARAMETER	FINAL AVERAGE CONCENTRATION IN UG/L (AVERAGE PERCENT CHANGE)				
	NONDISIN. GAC EFFL.	OZONE GAC EFFL.	CHLORINE DIOXIDE GAC EFFL.	CHLORAMINE[1] GAC EFFL.	CHLORINE GAC EFFL.
TOC[2]	2199(-39%)	1628(-56%)	2120(S)[3]	2111(S)	2070(S)
TOX[2]	14(-42%)	9.1(-52%)	24(NC)[4]	31(NC)	58(+43%)
TFIC[6,7]	1.5(54%)	1.6(S)	1.5(S)	1.7(S)	1.7(S)
THM[2]	0.6(NC)	0.5(NC)	0.6(NC)	4.6(NI)[5]	34(NI)
1,2-dichloroethane[2]	03(-35%)	0.2(S)	0.3(S)	0.3(S)	0.6(NC)
Total alkylbenzene	0.063(-46%)	0.074(S,NI)	0.079(S)	0.077(S)	0.077(S)
TECC[6,8]	0.074(-79%)	0.090(S)	0.098(S)	0.245(-29%)	0.604(+43%)
Total phthalate	0.117(-51%)	0.155(S)	0.093(S)	0.123(S)	0.115(S)
Total PNAH	0.028(-74%)	0.026(S,NI)	0.027(S)	0.028(S)	0.027(S)
alachlor	0.003(-93%)	0.002(S)	0.001(S)	0.002(S)	0.001(S)
Total chlorobenzne	0.005(-95%)	0.005(S)	0.004(S)	0.005(S)	0.004(S)
atrazine	0.004(-92%)	0.002(S)	0.002(S)	0.002(S)	0.002(S)
4-nonylphenol	0.008(-75%)	0.006(S,NI)	0.006(S)	0.007(S)	0.006(S)
Total alkane	0.018(-52%)	0.018(S)	0.020(S)	0.019(S)	0.018(S)
tributylphosphate	0.003(-94%)	0.001(S)	0.001(S)	0.001(S)	0.001(S)
Total CHI	0.003(-90%)	0.002(S)	0.002(S)	0.002(S)	0.003(S)
Total nitrobenzene	0.002(-96%)	0.001(S)	0.002(S)	0.002(S)	0.003(S)
Total alkylaldehyde	0.011(NC)	0.013(NC)	0.011(NC)	0.011(NC)	0.011(NC)
d-fenchone	0.000(-89%)	0.000(S)	0.002(-66%)	0.000(S)	0.001(S)
triphenylmethane	0.001(-53%)	0.001(S)	0.001(S)	0.001(S)	0.001(S)

---

[1] The majority of those by-products formed are attributable to a brief contact with free chlorine.

[2] Parameters exhibiting breakthrough curves. The benefit of GAC filtration has been reduced significantly because of operation after a "saturation" or "steady state" condition has been reached.

[3] Similiar to the removal observed for the nondisinfected GAC columns.

[4] No significant change relative to the nondisinfected influent.

[5] No significant change relative to the respective column influent.

[6] Averages for the last 210 days of the operational period.

[7] Quantitated as 1-chlorododecane.

[8] Quantitated as endosulfan-I.

due to the erratic nature of some of the data. This was particularly true for the flame ionization detectable substances in the effluent of the sand columns since these were monitored on a biweekly basis as opposed to weekly basis for the other process locations.

When comparing these tables one should bear in mind that the majority of the increases in concentration observed for the chloramine process stream were attributable to a brief contact with free chlorine during the generation of chloramines. Analytical evidence has indicated that these increases can be virtually eliminated by forming chloramines prior to injection into the process stream. However, one must also consider the report by Scarpino[9] which indicates that preformed chloramines are 20% less effective against E. Coli than chloramines formed in the process stream from the addition of ammonia followed by chlorine. It should also be noted that the benefits of GAC filtration for those parameters indicated in Table 33 as having had a typical breakthrough curve, have been greatly understated in this table due to the operation of these GAC columns beyond the point of "saturation" or "steady state". However, the relative effectiveness of each process stream for the removal of these substances remains evident.

An evaluation of the average annual effects of the alternative disinfectants after 30 minutes of disinfectant contact time in Table 31 indicate that the stronger oxidants produced greater changes in the levels of dissolved organics. The relative oxidation potentials of the alternative disinfectants are ozone > chlorine > chlorine dioxide > chloramine[1]. The greatest difference relative to the dissolved organic content was observed between the two strongest oxidants with ozone producing a large number of reductions while chlorine produced a considerably large number of increases. In general, ozonation produced dissolved organic reductions ranging from 9-89% while the increases observed for chlorination ranged from 43-2515%. Both chlorine dioxide and chloramine, having considerably lower oxidation potentials, produced considerably lower increases in the concentrations of dissolved organic substances. Thus, it would appear that the best pretreatment for the removal of dissolved organics was ozonation with the next best pretreatment being no pretreatment at all. While ozonation exhibited true reductions of all of the surrogate parameters (TOC, TOX, TFIC, and TECC), it is unclear whether or not all of the specific organics indicated were destroyed or merely transformed upon reaction with ozone. It is evident that some were destroyed as indicated by the reductions in the surrogate parameters. However, it is also evident that others were created as evidenced by the low levels of alkylaldehydes formed. It is further evident that other substances were transformed making them more susceptible to natural chemical and biological degradation as indicated by the additional 15% reduction in TOC observed across the ozone sand column while only a 1.5% reduction was observed across the nondisinfected sand column. However, the majority of the reduction observed appears to be that of the natural occurring organic substances as opposed to synthetic organic substances, since few of the specific organic substances monitored exhibited additional reductions across the ozone sand column. Also, it should be noted that it is unlikely that all of the ozonation by-products were observed, as well as those of the other disinfectants, since the extraction methology used was not suitable for the recovery of the more water soluble by-products.

The examination of the average concentrations of dissolved organics in the sand column effluents in Table 32 reveals that the only significant reduction of 0.5 mg/l was observed for TOC across the ozone sand column. As indicated earlier, this reduction was attributable to biological degredation. Several additional reductions were observed across the nondisinfected and ozone sand columns while a few reductions were also observed across the chlorine dioxide and chloramine sand columns. Significant reductions in TFIC, total alkylbenzene, total phthalate, and total chlorobenzene were observed across the chlorine sand column, however these effluent levels remained considerably higher than those of the other process streams. In addition, the level of THM's increased from an average of 34 ug/l to 50 ug/l across the chlorine sand column resulting from additional chlorine contact time with THM precursor material.

Similiar trends relative to the removal of dissolved organics were observed for GAC filtration as indicated in Table 33 with the major differences being observed for the surrogate parameters and volatile organics while essentially the same reductions were observed for the specific semivolatile organics in all process streams. The average reductions observed for the nondisinfected GAC columns ranged from 0-95%. Relative to these nondisinfected GAC removals, the ozone GAC columns exhibited greater reductions in TOC and TOX while the poorest reductions for TOX, TECC, THM's, and 1,2-dichloroethane were observed for the GAC columns of the chlorine process stream. Lower average reductions in TOX and d-fenchone were observed for the GAC columns of the chlorine dioxide system relative to those of the nondisinfected GAC columns. While the reductions observed for the chlorine dioxide and chloramine GAC columns were fairly similiar, slightly lower removals were observed for TOX, THM's, and TECC across the chloramine GAC columns due to the brief presence of free chlorine during the generation of chloramines.

At this point it should be noted that those average concentrations indicated in Table 33, in many instances, are not indicative of the final concentrations which would be received by the consumer. The reason being that there was no post disinfectant applied which would maintain a significant disinfectant residual in the distribution system. While there were some formation potential evaluations performed, these data are not indicative of the distribution system water quality because of the considerably higher levels of disinfectants applied. Because ozone and chlorine dioxide dissipate rather rapidly, only chloramines and free chlorine appear to be suitable for maintaining a disinfectant residual in the distribution system. An examination of Table 31 suggests that chloramines would be more suitable since they produce fewer dissolved organic substances. Chloramines are also more stable than free chlorine and will thus maintain a residual for a longer period in the distribution system. While chloramines possess a lower oxidation potential than does free chlorine and are thus less reactive, chloramines function quite well in maintaining a high bacteriological water quality within the distribution system.[1] Jefferson Parish has used chloramines as our primary and sole disinfectant for over 30 years with good results.[10] A complete evaluation of the two best pretreatments (ozone and no predisinfection) in conjunction with GAC filtration and post disinfection will be described in a subsequent report entitled "Optimizing Trace Organics Removal through Preozonation, Granular Activated Carbon, and Postchloramination".

REFERENCES

1 Koffskey, Wayne E. and Brodtmann, Noel V., Organic Contaminant Removal in Lower Mississippi River Drinking Water by Granular Activated Carbon Adsorption, EPA-600/52-83-032, June 1983.

2 White, George Clifford, Handbook of Chlorination, Van Nostrand Reinhold, New York, 1972.

3 Coleman, W. E. et al, Determination of Organic Contaminants by the Grob Closed Loop Stripping Technique, JAWWA 73:119, 1981.

4 Federal Register, Vol. 49, No. 209, October 26, 1984.

5 Standard Methods for the Examination of Water and Wastewater, 15th Edition, 1980.

6 Aieta, E. Marco; Roberts, Paul V.; and Hernandez, Margarita, Determination of Chlorine Dioxide, Chlorine, Chlorite, and Chlorate in Water, JAWWA 76:64, 1984.

7 Fleishcacker, Stephen J. and Randtke, Stephen J., Formation of Organic Chlorine in Public Water Supplies, JAWWA 75:132, 1983.

8 Fochtman, Edward G., Biodegradation and Carbon Adsorbtion of Carcinogenic and Hazardous Organic Compounds, EPA-600/S2-81-032, March 1981.

9 Scarpino, Pasquale V., Effect of Particulates on Disinfection of Enteroviruses in Water by Chloramines, EPA-600/S2-84-094, September 1984.

10 Brodtmann, Noel V.; Koffskey, Wayne E.; Demarco, Jack; Studies of the Use of Combined Chlorine (Monochloramine) As A Primary Disinfectant of Water Treatment, Water Chlorination 3:777.

APPENDIX

GRANULAR ACTIVATED CARBON SELECTION

An evaluation of various types of GAC was conducted to determine which type of GAC exhibited the best overall performance under the organic load present in lower Mississippi River water. The types of GAC that were evaluated during this trial are presented in Table 1. The operational period of this trial was approximately six months in duration, beginning on January 7, 1981 and ending on July 1, 1981.

The parameters monitored and used for this evaluation were empty bed contact time (EBCT) and the influent and effluent levels of: total organic carbon (TOC), instantaneous trihalomethanes (THM-I), terminal trihalomethanes (THM-FP), 1,2-dichloroethane (DCE), electron capture total area (ECTOAR), flame ionization total area (FITOAR), and heterotrophic plate count (HPC). In the determination of terminal trihalomethanes, the samples were incubated for five days at ambient water temperature after an addition of free chlorine such that the concentration in solution was 10 mg/l. In order to evaluate the adsorption of known as well as unknown organic species that were detectable by gas chromatography, ECTOAR and FITOAR parameters

---

TABLE 1. TYPES OF GAC UNDER EVALUATION.

MANUFACTURER	TRADE NAME	MESH SIZE	DRY DENSITY (lb/cu.ft.)
Calgon	Filtrasorb 400	12 x 40	27.5
Carborundum	GAC 40	12 x 40	27.5
ICI	Hydrodarco 4000	12 x 40	27.5
Norit	ROW 0.8 Supra	0.8mm dia.[a]	22.5
Westvaco	WV-G	12 x 40	27.5

---

[a] pelletized GAC-0.8mm dia. cylinders varying in length from 1-2 mm.

were developed which incorporated the total area under the chromatogram (excluding the solvent front) of the sample as compared to that of the external standards in the daily standard chromatogram. The gas chromatographs used were operated at 180°C isothermal for ECTOAR and 40-220°C at 4°C/min with a 10 min hold at 40°C for FITOAR. Both ECTOAR and FITOAR analyses used 60m SE-30 glass capillary columns and the duration of each analysis was two hours.

The sampling frequency was once each week for TOC, THM-I, DCE, HPC, ECTOAR and FITOAR and once every two weeks for THM-FP. Pilot column flow rates or EBCTs were monitored daily (excluding weekends). If a flow rate adjustment was required on a sampling day, samples were not collected until after the adjustments were made and at least one bed volume of water had passed through the column. All analyses were performed in duplicate except for ECTOAR and FITOAR.

OPERATING CONDITIONS

The various types of GAC under evaluation in this trial were placed in 3 in. or 4 in. dia. by 6 ft. glass columns to a depth of 30 inches. All wetted pilot column system components were comprised of stainless steel, cast aluminum, teflon, or glass. These columns were operated at a hydraulic loading of 1.25 GPM/ft^2 or 15 min. EBCT. No backwashing of any of the GAC columns occurred during the operational period and thus no carbon losses were incurred. The variations in the daily flow rates observed and those that were set are presented in Figure 1 while the average daily flow rates (between that observed and that set the previous day) are presented in Figure 2. A pump failure occurred around day 22 as indicated by the large surge in Figure 2. As indicated in the legends of both of these figures, the overall average EBCTs for each type of GAC did not deviate from one another more than 0.29 minutes. This deviation is quite small and therefore any effect this may have had relative to adsorption performance is considered to be negligible. This assumption was supported by the data in that a carbon type with a longer average EBCT did not always exhibit a higher adsorption efficiency.

The build-up of bacteria on the carbon surface in each column as indicated by the HPC from the effluent of each column is depicted in Figure 3. The trends shown for each GAC column, in biological terms, are essentially identical, each having risen approximately three orders of magnitude in 30-40 days to above 10,000 CFU/ml which was followed by a slow decline after 90 days to 100-1000 CFU/ml.

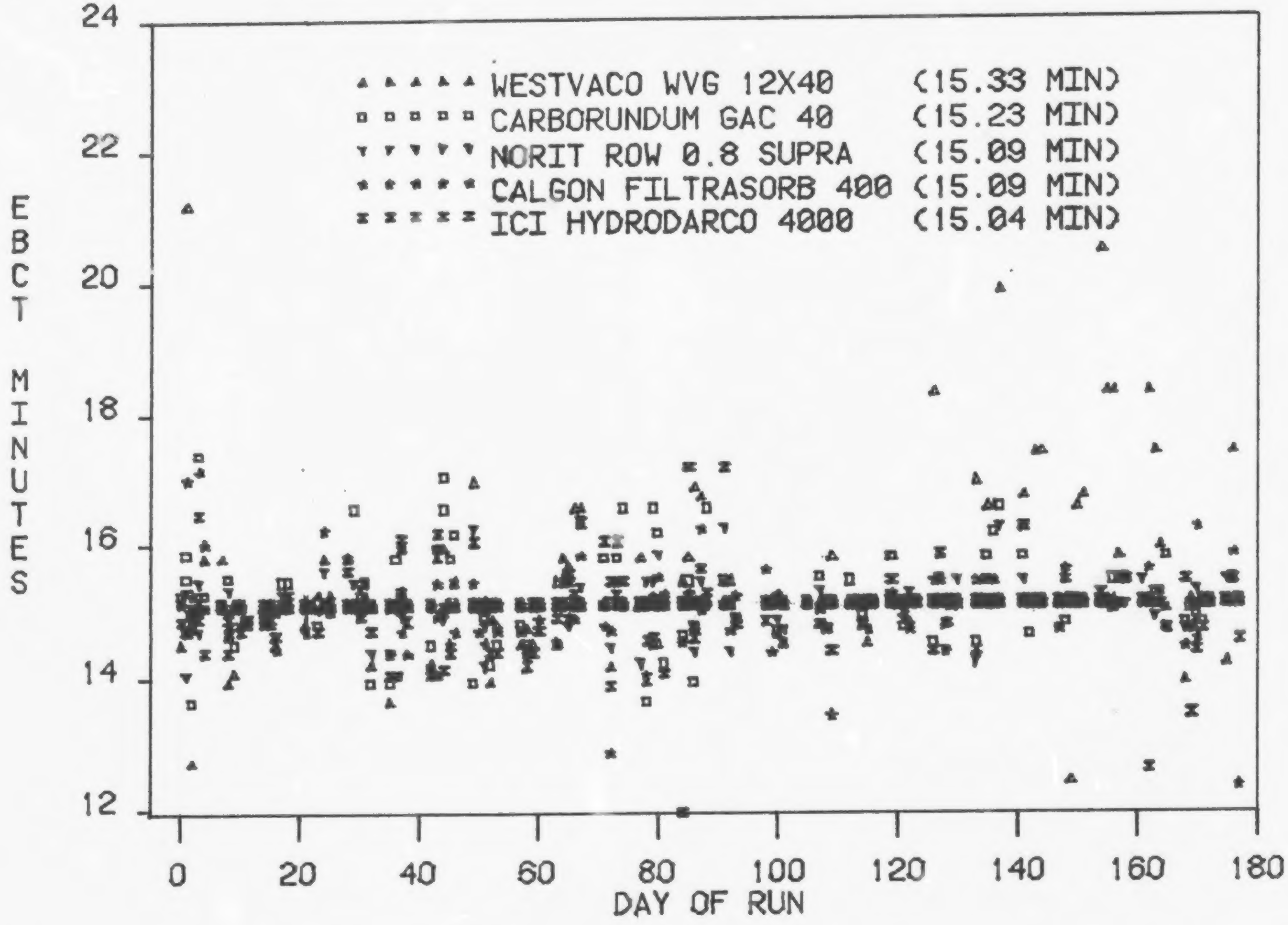


FIGURE 1: Daily EBCTs observed and set for each type of GAC.

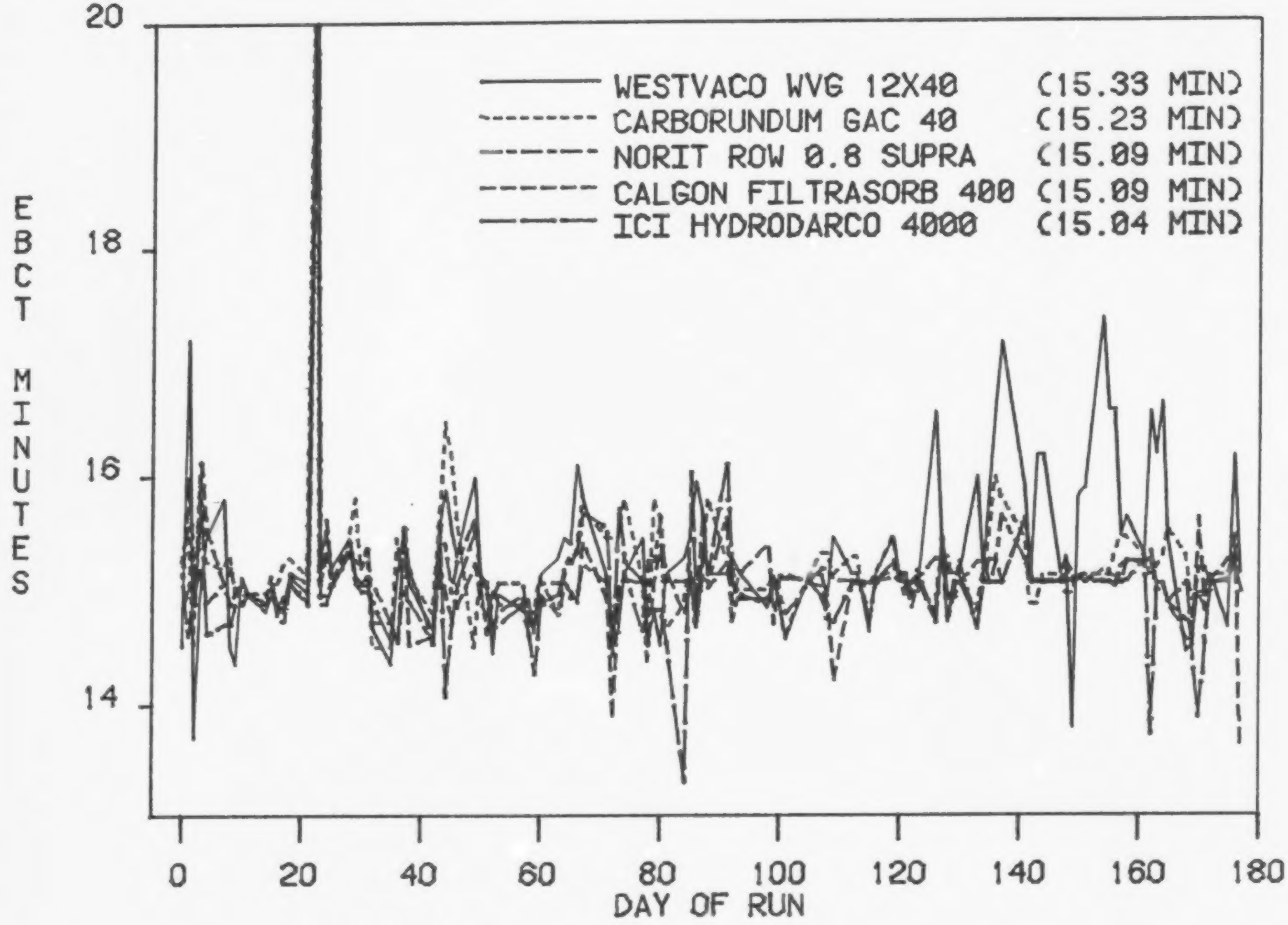


FIGURE 2: Average daily EBCTs observed for each type of GAC.

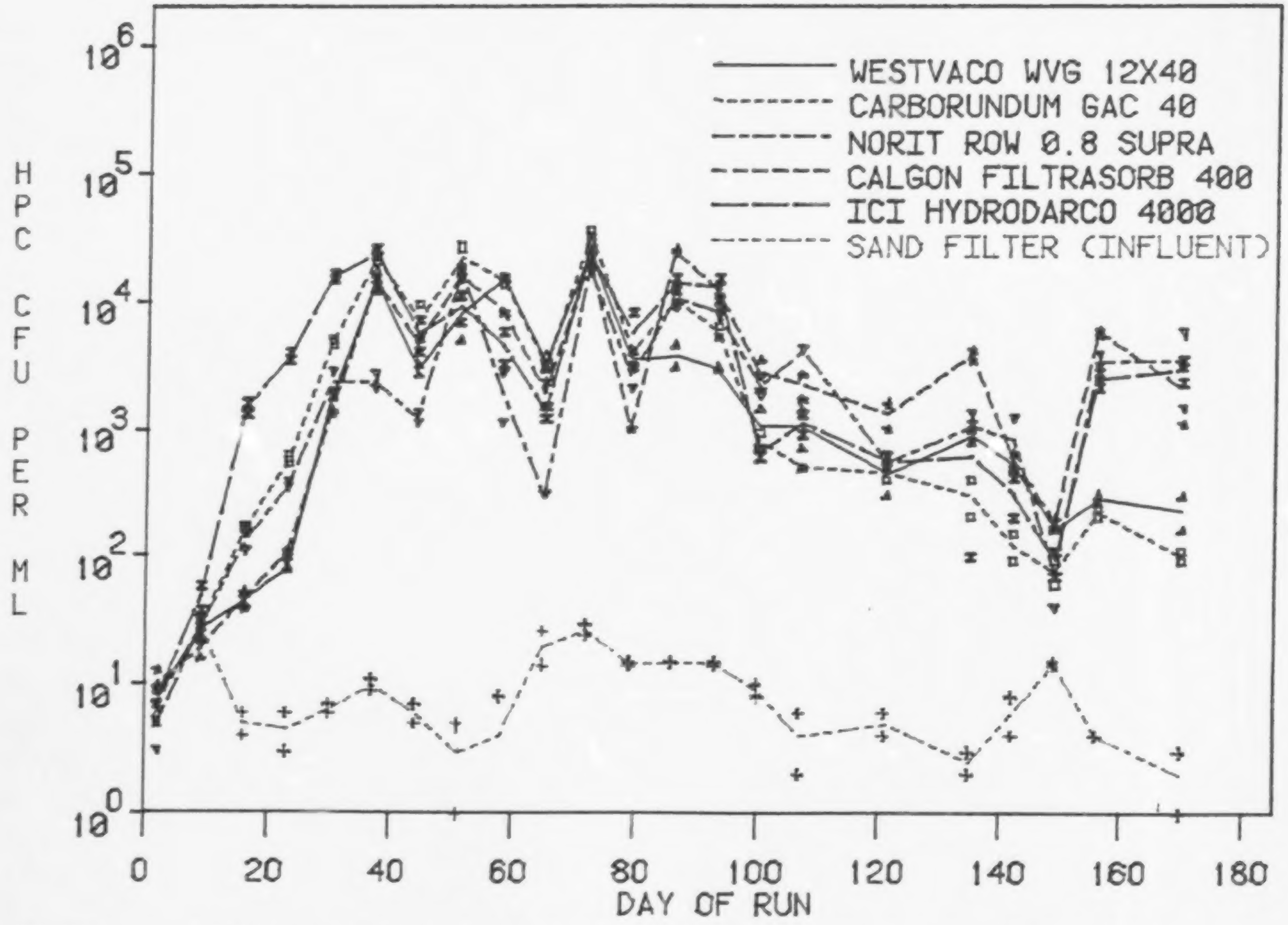


FIGURE 3: Effluent Heterotrophic Plate Counts (HPC) for each carbon type.

Thus, the peformance of each type of GAC is considered to be directly comparable since each pilot column was operated with essentially the same EBCT, received the same influent water and supported a relatively similiar level of heterotrophic bacteria.

The water entering each column was fully processed water which had been clarified by diallyldimethylammonium chloride and/or dimethylamine polymers, disinfected with monochloramine, sand filtered and had received an addition of a zinc-sodium hexametaphosphate corrosion inhibitor. Typical influent water quality for the pilot column system is presented in Table 2.

RESULTS AND DISCUSSION

Prior to start-up of the operational period, the initial organic load on each type of GAC was examined by the Soxhlet extraction of 60 grams of carbon with hexane for 8 hours. While the electron capture chromatograms showed essentially no contamination, a considerable amount of contamination was evident on the flame ionization chromatograms. Examination of these chromatograms indicated the following levels of contamination: Hydrodarco 4000 >>> WV-G > ROW 0.8 Supra >> GAC 40 > Filtrasorb 400. It was not surprising that Hydrodarco 4000 was the most contaminated carbon as upon concentration of the extract, a significant amount of (0.02% by weight) of what appeared to be sulfur precipitated from solution. However, it would appear from the results that the degree of initial organic contamination had no discernable effect on adsorption performance as the second most contaminated GAC, WV-G, exhibited the highest overall performance.

TOC:

Profiles of effluent TOC for each type of GAC are depicted in Figure 4. The bituminous carbons appeared to have been more efficient than the lignite carbon (Hydrodarco 4000), having exhibited effluent concentrations that were consistently 0.5 mg/l below that of the lignite carbon. Westvaco's WV-G appeared to have been the most efficient of the bituminous carbons, however, this is fairly difficult to observe due to the somewhat erratic nature of the data combined with relatively small differences in effluent concentration. This is, however, observable in the average TOC effluent concentrations across the operational period as follows: WV-G, 2.14 mg/l; GAC 40, 2.33 mg/l; Filtrasorb 400, 2.36 mg/l; ROW 0.8 Supra, 2.42 mg/l; and Hydrodarco 4000, 2.87 mg/l.

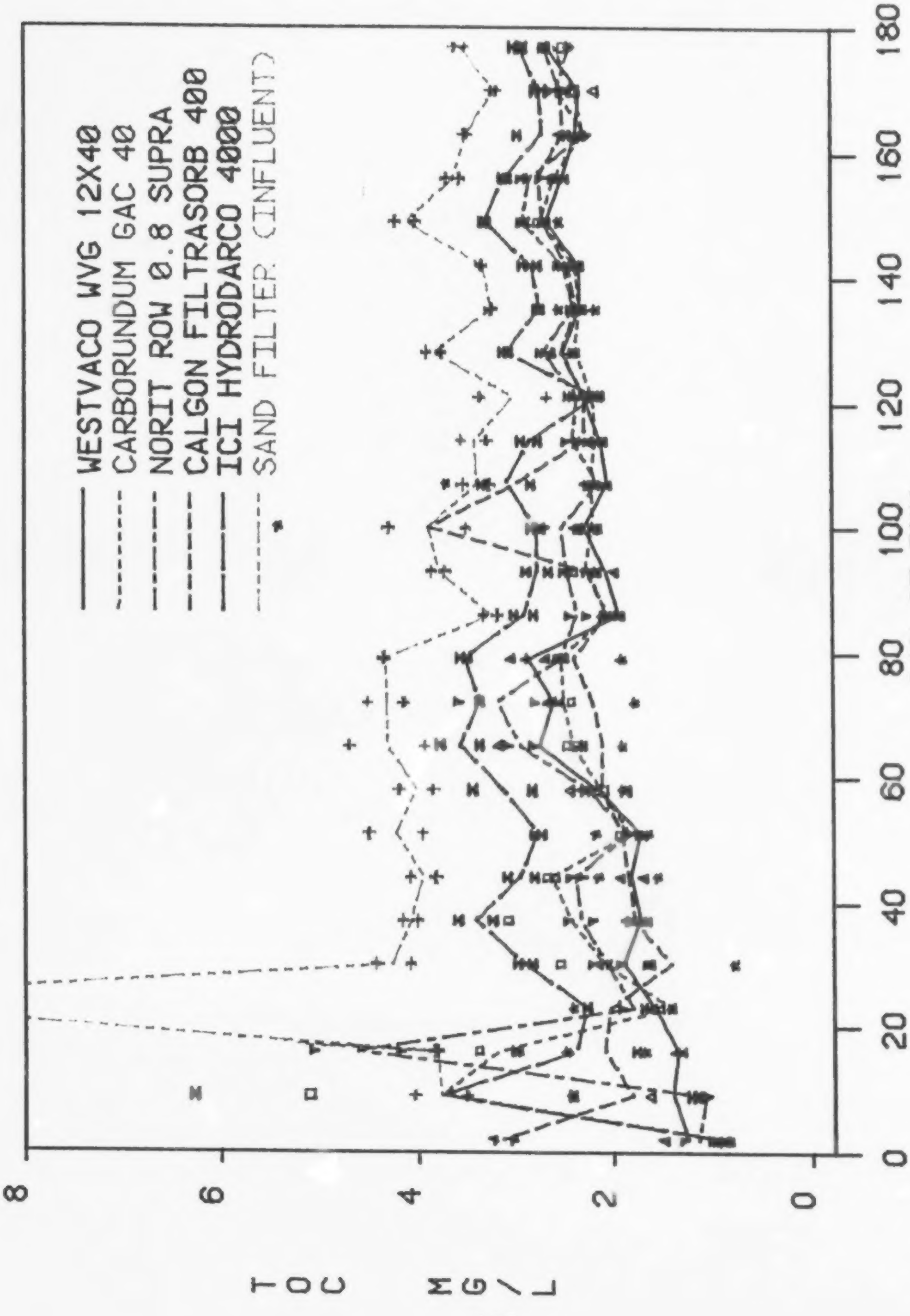


FIGURE 4: Effluent TOC concentrations for each type of carbon.

TABLE 2. TYPICAL INFLUENT WATER QUALITY[a]

PARAMETER	MINIMUM	AVERAGE	MAXIMUM
carbonates	0	0	0
bicarbonates	52	95	125
hydroxides	0	0	0
calcium	23	35	78
total hardness	86	131	180
pH	7.0	7.4	7.9
monochloramine residual	1.0	1.6	2.2
turbidity (NTU)	0.01	0.5	1.1
total dissolved solids	90	209	400
temperature (°C)	3	18	31

---

[a] units are mg/l unless otherwise specified.

THM-FP:

The same conclusions that were drawn for TOC, relative to adsorption performance, can be drawn for THM-FP, however, the differences between the various GAC types are more visible for this parameter in Figure 5 due to the less erratic nature of these data. The relative performances of these various carbons relative to THM-FP are identical to those of TOC as indicated by their average effluent concentrations as follows: WV-G, 128 ug/l; GAC 40, 135 ug/l; Filtrasorb 400, 157 ug/l; ROW 0.8 Supra, 164 ug/l; and Hydrodarco 4000, 236 ug/l.

THM-I:

The THM-I effluent concentrations of each type of GAC presented in Figure 6 indicate that each carbon type reached saturation at roughly the same time, between day 110 and day 115. However, this is believed to have been caused by the relatively large surge in influent concentration which occurred around day 104 which was the result of a partial loss of ammonia feed causing the presence of some free chlorine. It is unfortunate that this relatively large increase in influent concentration occurred at the same time as the effluent concentrations of each of the GAC columns were approaching saturation. This influent surge most probably resulted in the premature saturation of each carbon column making the differences in their saturation points difficult to observe. However, even with this surge in influent

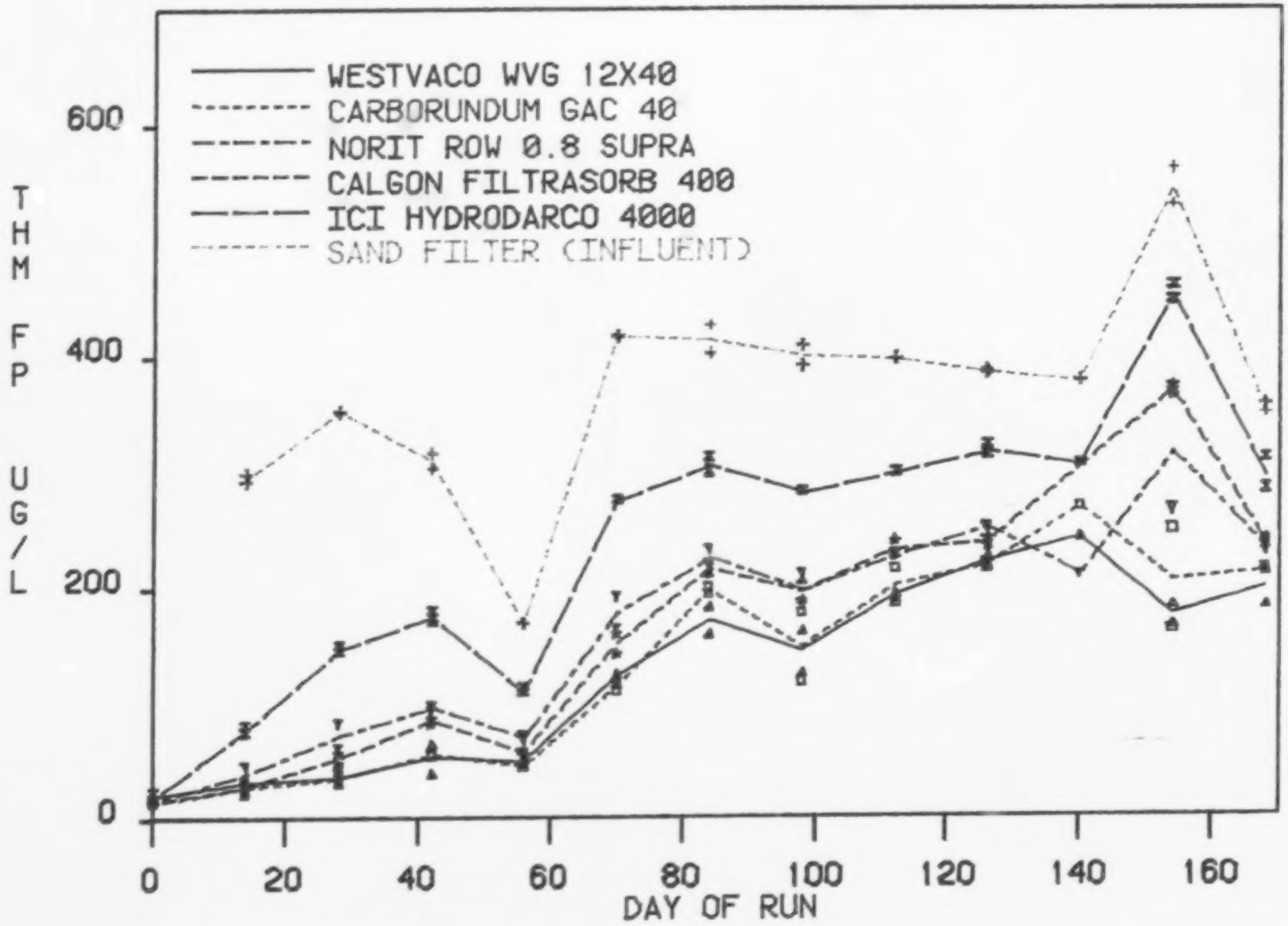


FIGURE 5: Effluent THM-FP concentrations for each type of carbon.

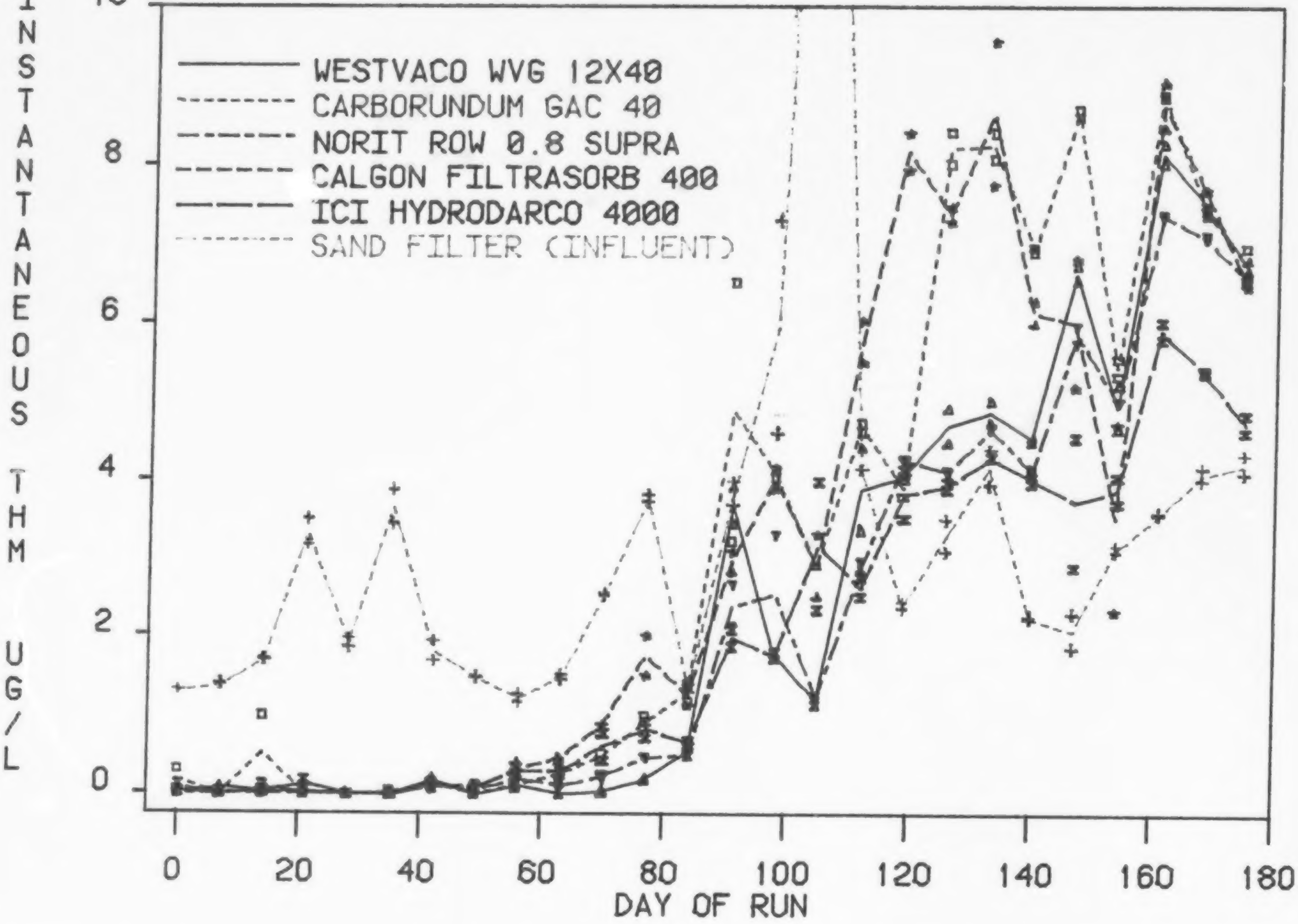


FIGURE 6: Effluent THM-I concentrations for each type of carbon.

concentration, the data presented in Figure 6 indicates that WV-G, ROW 0.8 Supra and Hydrodarco 4000 exhibited a somewhat better adsorption efficiency than did Filtrasorb 400 and GAC 40. This is also somewhat evident prior to the occurrance of the influent surge and is further evident in the higher levels of desorption which occurred for Filtrasorb 400 and GAC 40 after saturation.

DCE:

As was the case for THM-I, all of the GAC columns reached saturation within a relatively short period of time, between day 60 and day 80, which may have resulted from an earlier surge in influent concentration as indicated in Figure 7. These surges in DCE concentration have been frequently observed in the influent river water and have been associated with variations of industrial discharges into the Mississippi River upstream of our location. Similiar to that of THM-I, Figure 7 indicates that the adsorption efficiencies of WV-G, ROW 0.8 Supra and Hydrodarco 4000 were superior to those of Filtrasorb 400 and GAC 40 in that the latter two carbons reached saturation about 18-21 days earlier and exhibited a significantly higher level of desorption after saturation.

ECTOAR AND FITOAR:

Electron capture total area and flame ionization total area effluent profiles are presented in Figures 8 & 9. These data indicate that there was relatively little difference in the adsorption efficiencies of the various carbon types with respect to these two parameters. It is interesting to note, however, the relative lack of adsorption efficiency in the FITOAR profiles in Figure 9 which occurred at the lower influent levels and would indicate that these types of compounds had a lower affinity for GAC than did the halogenated compounds depicted in the ECTOAR profiles in Figure 8.

CONCLUSIONS

In summary, Westvaco's WV-G exhibited the highest adsorption efficiency for each parameter monitored during this study and as such should be considered the carbon of choice for the removal of trace organics from lower Mississippi River water. Each of the other GAC types exhibited some deficiency in TOC, THM-FP, THM-I and/or DCE adsorption efficiency.

The second choice of carbon for this application would be Carborundum's GAC 40 which adsorbed TOC and THM-FP almost as well

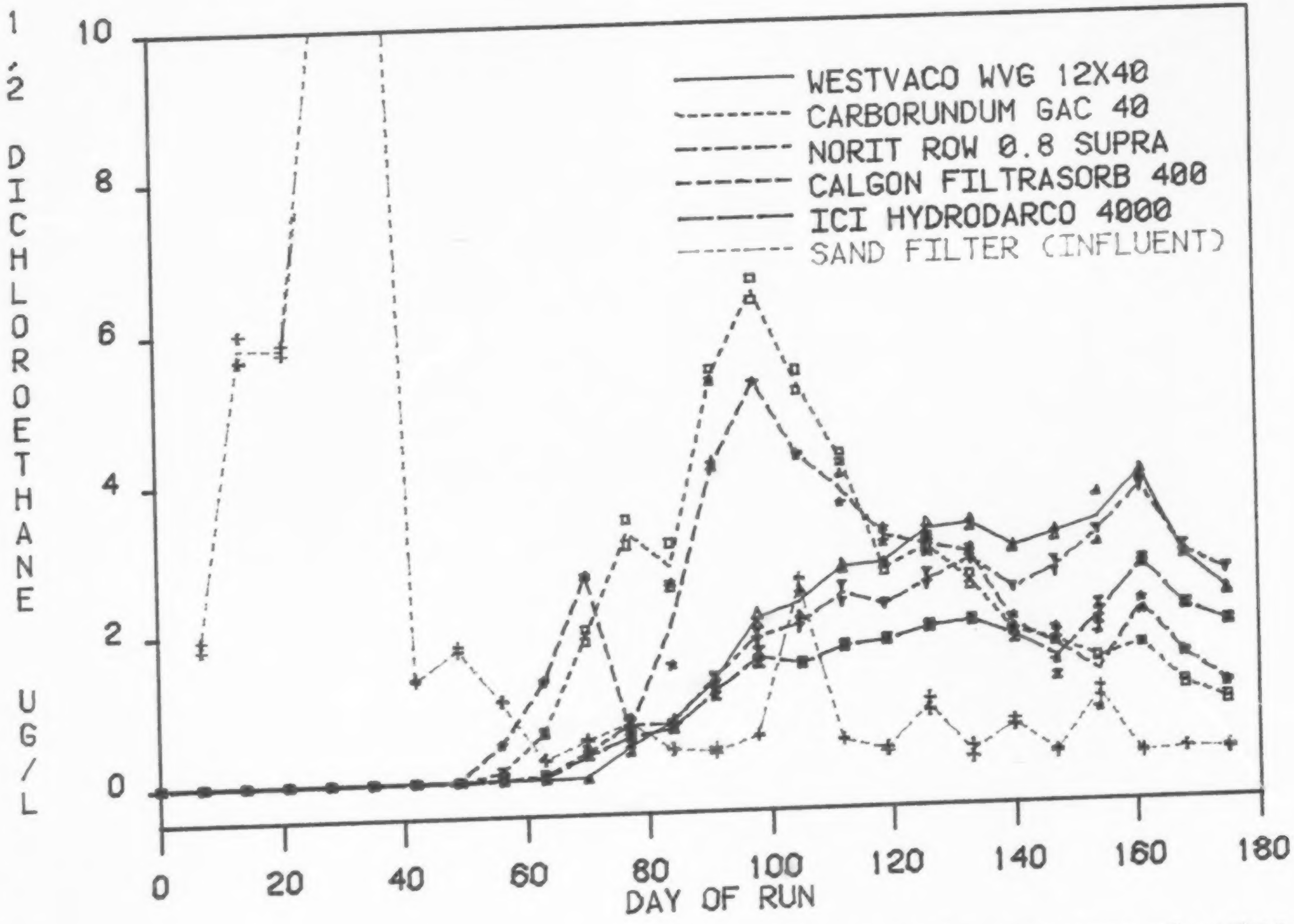


FIGURE 7: Effluent 1,2-Dichloroethane (DCE) concentrations for each type of carbon.

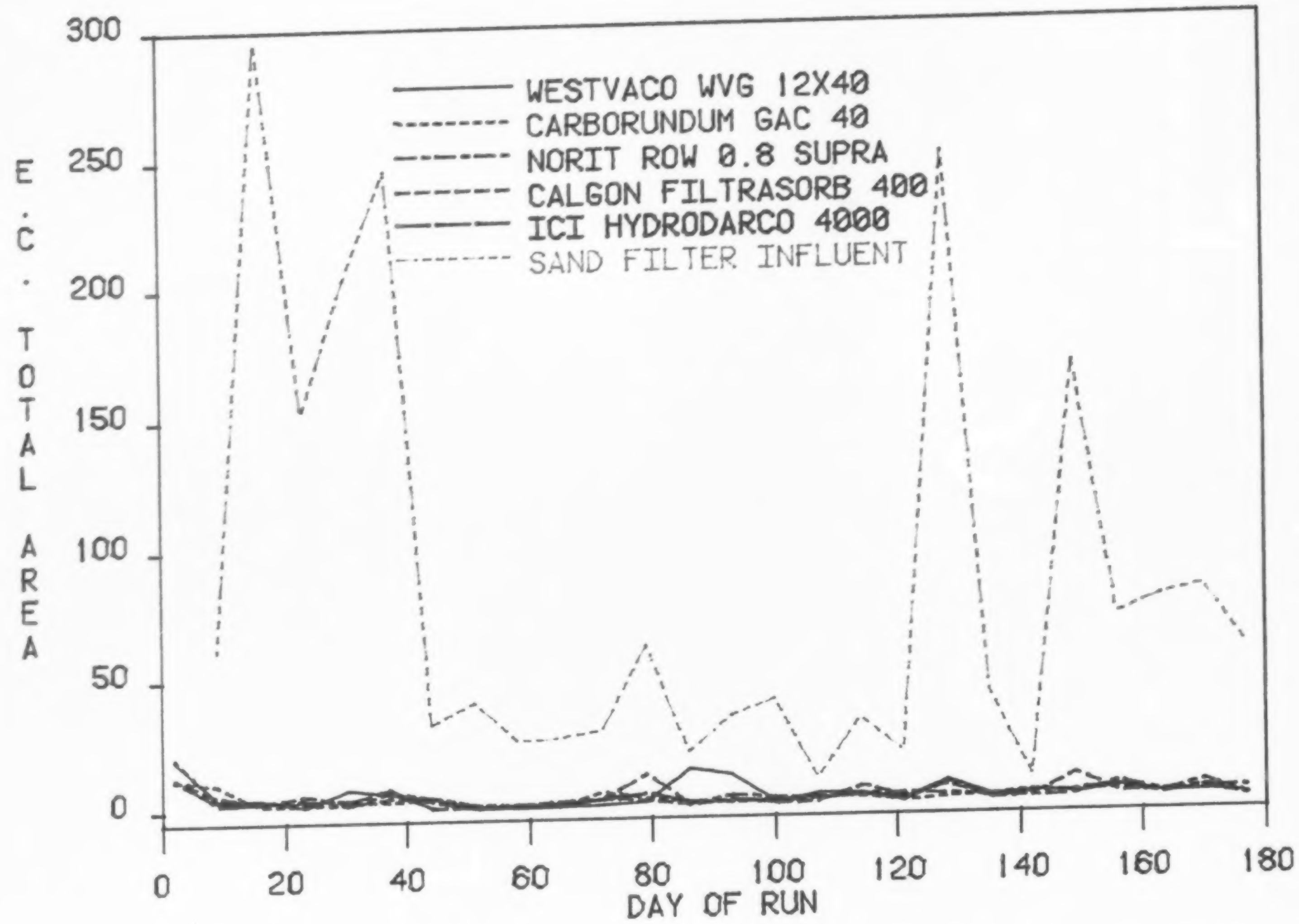


FIGURE 8: Effluent Electron Capture Total Area (ECTOAR) for each type of carbon.

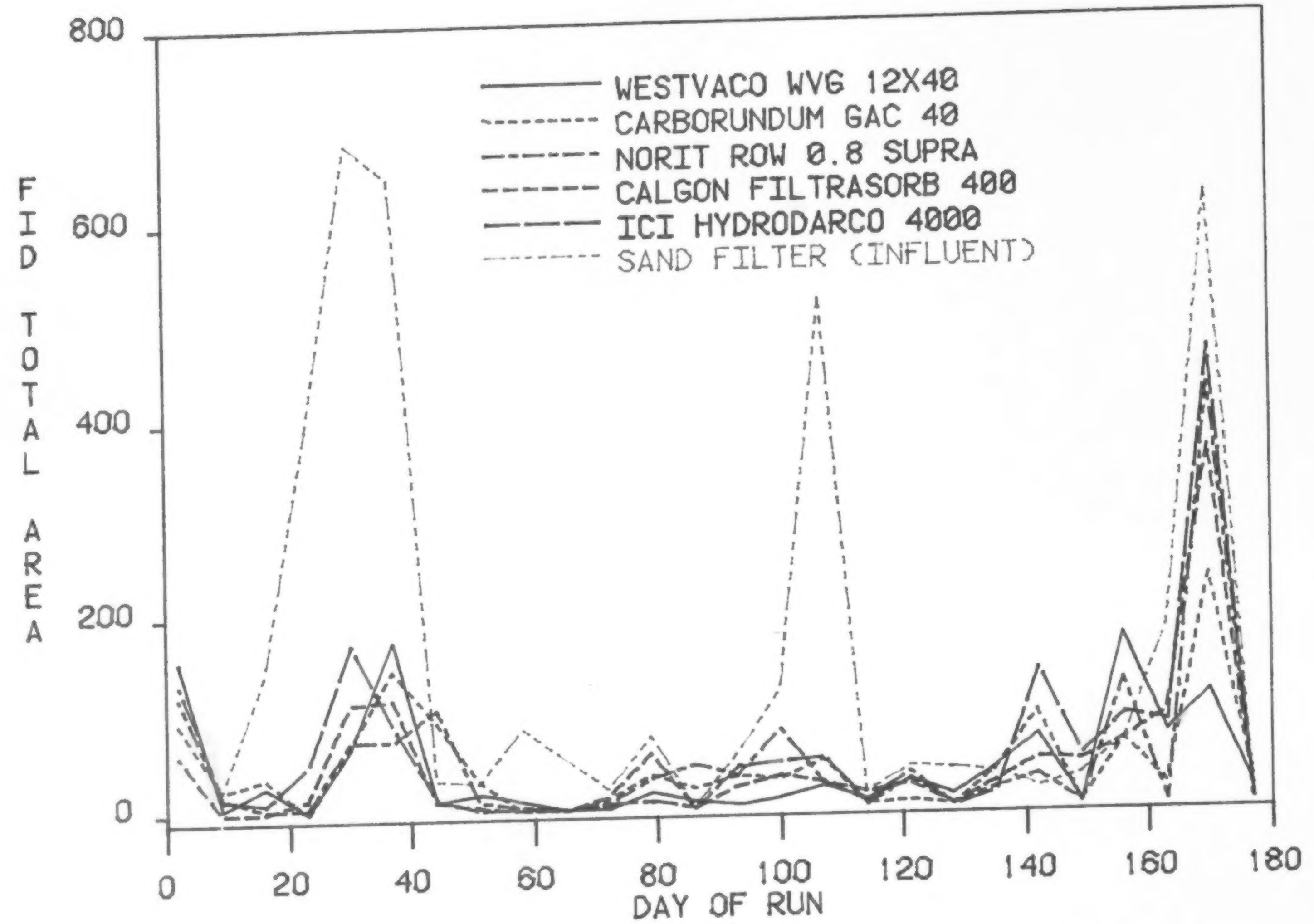


FIGURE 9: Effluent Flame Ionization Total Area (FITOAR) for each type of carbon.

as WV-G with saturation occurring only about 7 days before WV-G for THM-I at the 4 ug/l level and about 21 days earlier than WV-G for DCE at the 0.5 ug/l level. Due to the low levels of occurrance of these lower molecular weight species (THM-I and DCE) in our water treatment system, the removal of the wider spectrum higher molecular weight species encompassed by TOC and THM-FP is considered to be of higher importance.

The adsorption efficiencies of the other three carbons under study varied somewhat relative to the various parameters monitored. Calgon's Filtrasorb 400 exhibited relatively good adsorption efficiency for TOC although it was somewhat less than that of WV-G and GAC 40, and a considerably poorer adsorption efficiency for THM-FP, THM-I and DCE. Norit's Row 0.8 Supra performed similiar to that of Filtrasorb 400 for TOC and THM-FP while its adsorption efficiency was similiar to that of WV-G for THM-I and DCE. One other consideration in the use of Norit ROW 0.8 Supra is that due to its somewhat smaller particle size and lower density, the backwash free board for a system using this carbon in conventional filters would have to be greater than that for the other denser carbons. The adsorption efficiency exhibited by ICI's Hydrodarco 4000 was very poor for TOC and THM-FP, however, it was equivalent to that of WV-G for THM-I and DCE. Also, virgin Hydrodarco 4000 was observed to contain what appeared to be 0.02% by weight of hexane-extractable sulfur.